U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-286 241

Mass Balance Determinations for Pollutants in Urban Regions. Methodology with Applications to Lead, Zinc, Cadmium, and Arsenic

California Inst. of Technology, Pasadena

Prepared for

Environmental Monitoring and Support Lab., Las Vegas, NV

Aug 78

United States
Environmental Protection
Agency

Environmental Monitoring
and Support Laboratory
P.O. Box 15027
Las Vegas NV 89114

EPA-600/4-78-046
August 1978

Research and Development

PB 286 241

EPA

Environmental Monitoring Series

Mass Balance Determinations for Pollutants in Urban Regions

Methodology with Applications to Lead, Zinc, Cadmium, and Arsenic

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-78-046	2.	3. RECIPIENT'S ACCESSION NO. PB286241
4. TITLE AND SUBTITLE MASS BALANCE DETERMINATIONS FOR POLLUTANTS IN URBAN REGIONS Methodology with Applications to Lead, Zinc, Cadmium, and Arsenic		5. REPORT DATE August 1978
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Department of Environmental Health Engineering		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS California Institute of Technology Pasadena, California 91125		10. PROGRAM ELEMENT NO. 1HD620, 1HD622
		11. CONTRACT/GRANT NO. 68-03-4034
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency-Las Vegas, NV Office of Research and Development Environmental Monitoring and Support Laboratory Las Vegas, NV 89114		13. TYPE OF REPORT AND PERIOD COVERED Special Report
		14. SPONSORING AGENCY CODE EPA/600/07

15. SUPPLEMENTARY NOTES This project was partially funded by EPA's Technology Transfer Office under the Environmental Research Information Center, Cincinnati, Ohio.

16. ABSTRACT

A methodology is presented for constructing mass balances for pollutants which move interactively through the air, land, and water of an urban-industrial region. Results are reported for lead, zinc, cadmium, and arsenic based on experiments conducted specifically for this study, and on available data from the open literature. The principle on which the analysis is based is the conservation of mass equation for a given chemical element. Using chemical element balance as in flow diagrams for the movement of pollutants through the environment, rates of flow and accumulation can be estimated for the separate environmental compartments.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollutant inventories	Mass balances	13B
Chemical balances	Pollutant pathways	07B
Particle size-distribution	Particle dispersion	
Systems analysis	Transport of lead, zinc, cadmium and arsenic	

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 126
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE MF A01 PC A07

EPA-600/4-78-046
August 1978

MASS BALANCE DETERMINATIONS FOR POLLUTANTS IN URBAN REGIONS
Methodology with Applications to Lead, Zinc, Cadmium, and Arsenic

by

Department of Environmental Health Engineering
California Institute of Technology
Pasadena, California

Contract No. 68-03-4034

Project Officer

Edward A. Schuck
Monitoring Systems Research and Development Division
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory-Las Vegas, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Foreword

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs.

This report discusses a methodology for constructing mass balances for pollutants which move interactively through the air, land, and water of an urban-industrial region. The method was developed for application in determining the fate of potentially toxic substances which may be conserved in the environment. Such application will be useful to State and local pollution control agencies in designing monitoring systems for determining pollutant levels in various environmental compartments. The Monitoring Systems Design and Analysis Staff at this Laboratory may be contacted for further information on the subject.

George B. Morgan

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada

PREFACE

This report was edited by personnel at the U.S. Environmental Protection Agency's Environmental Monitoring and Support Laboratory, Las Vegas (EMSL-LV) from a final report submitted to the EMSL-LV by the Department of Environmental Health Engineering at the California Institute of Technology (Caltech). The Caltech final report summarized work-to-date on area-wide mass balances techniques and included several papers which were published in the open literature that were authored by staff members of the Department of Environmental Health Engineering. Different portions of the original manuscript were written by C. I. Davidson, S. K. Friedlander, J. J. Huntzicker, R. C. Y. Koh, J. J. Morgan, J. Vucela, and N. H. Brooks.

CONTENTS

Foreword. iii
Preface iv
Figures vi
Tables. viii
Abbreviations ix

I. Introduction. 1
II. Summary 3
    Mass Balances for Trace Metals: State-of-the-Art . . 8
    Mass Balances for Trace Metals: Future Prospects . . 11
III. Relation Between Airborne Concentration and Deposition of Trace Metals 15
    Theory of Deposition 18
    Size Distributions 23
    Atmospheric Size-Distributions: Isokinetic Experiments 27
    Deposition of Lead, Zinc, and Cadmium 32
    Experimental Errors 37
    Andersen Impactor Cutoff Diameters 40
    Discussion of Trace-Metals Deposition Studies. . . . 42
IV. Examples of Mass Balances 44
    Automotive Lead in the Los Angeles Basin 44
    Lead in the Saline Branch Watershed of Illinois. . . 70
    Atmospheric Trace-Metal Flows in the Los Angeles Basin: Zinc and Cadmium. 71
V. Transport and Deposition through the Water Route. . . . 91
    Flows of Arsenic in the Southern California Water Environment 91
    The Ultimate Fate of Sewage Particulate Matter . . . 96
VI. Concluding Remarks. 105
VII. References. 106

FIGURES

Number		Page
1	Example of a flow diagram for automobile-emitted trace metals.	6
2	Airborne concentration of condensations nuclei as a function of height.	20
3	Data from figure 2, plotted on a logarithmic scale.	21
4	Total deposition of lead on Teflon plates at various heights	22
5	Normalized size distributions for lead, zinc and cadmium, based on aerodynamic equivalent diameters	30
6	Impactor stage collection efficiency as a function of particle diameter dp, for a typical stage	41
7	Cumulative mass distributions for lead aerosol in auto exhaust and in ambient air at Pasadena.	52
8	Differential mass distributions for lead at 1-meter from a freeway and for Pasadena.	53
9	Distribution of deposition factors in the Los Angeles Basin	55
10	Deposition of lead as a function of distance from the coast	60
11	The flow of automobile-emitted lead through the Los Angeles Basin	68
12	Differential mass distributions for zinc at 1-meter from a freeway and for Pasadena.	77
13	Deposition as a function of distance from a freeway for Pb, Zn, and Cd.	79
14	Zinc fluxes in the Los Angeles Basin	81
15	Deposition of Pb, Zn, and Cd as a function of distance from the coast	85

FIGURES (Continued)

Number		Page
16	Vertical distribution of particle concentrations at the centerline as a function of travel time	100
17	Measured and computer synthesized ocean current data off White's Point, California	103

TABLES

Number Page

1 Types of Information Necessary for Determining Fate of Airborne Trace-Metal Pollutants. 3

2 Percentage of Mass Greater Than 10 µm Aerodynamic Diameter for Nonisokinetic and Isokinetic Runs 28

3 Deposition Velocities of Lead 32

4 Calculated and Measured Fluxes to Flat Surfaces 35

5 Airborne Concentrations During the Two Isokinetic Impactor Experiments 35

6 Values of Mass Mean Cutoff Diameters dp_m and the Standard Deviations for the Andersen Impactor Efficiency Curves. . 41

7 Pb/CO at Various Sites in the Los Angeles Basin 58

8 Input of Anthropogenic Los Angeles Lead to the Coastal Waters. 64

9 Mass Balance for Automobile-Emitted Lead. 69

10 Zinc Content in Particulate Emissions from Metallurgical Operations. 73

11 Zinc to CO and Cadmium to CO Ratios in the Los Angeles Basin 76

12 Mass Balance for Zinc in the Atmosphere 80

13 Mass Balance for Cadmium in the Atmosphere. 84

14 Zn/Pb at Various Locations in the Los Angeles Area. 86

15 Deposition Ratios, August 1973. 87

16 Anthropogenic Inputs of Los Angeles Pb, Zn and Cd to the Coastal Waters. 89

17 Probability Definitions 102

ABBREVIATIONS

ACHEX -- California Aerosol Characterization Experiment
Caltech -- California Institute of Technology
cm/sec -- centimeters per second
CNC -- condensation nuclei counter
dp -- aerodynamic equivalent diameter
dp_{50} -- median aerodynamic equivalent diameter
dp_m -- mass mean cutoff diameters
g/l -- grams per liter
g/cm^3 -- grams per cubic centimeter
GDE -- General Dynamic Equation
km -- kilometers
m/sec -- meters per second
mm -- millimeter
MMED -- mass median equivalent diameter
μm -- micrometer and micron
$\mu g/m^3$ -- microgram per cubic meter
ng/cm^2 -- nanograms per square centimeter
nm -- nanometer
pdf -- probability density function
ppm -- parts per million
SCCWRP -- Southern California Coastal Waters Research Project
u^* -- friction velocity
v_g -- deposition velocity
v_s -- sedimentation velocity

Abbreviations are listed as used in this report and are not necessarily the recognized standard abbreviations. For example, micron and micrometer are used interchangeably in the text, paraphrasing original input data from the literature.

SECTION I

INTRODUCTION

Studies of pollutant flows through urban and industrial regions are potentially useful in a number of ways. They can help in the design of integrated monitoring systems for determining pollutant levels in various environmental compartments and for determining control systems for limiting pollutant exposures to prescribed levels. They can also be used to estimate the effects of urban areas on surrounding regions. This is of interest in the development of a rational nondegradation policy. Finally, such studies are needed to determine the fate of potentially toxic substances, such as certain trace metals, which are conserved in the environment.

This report is a review of the methodology which has been developed at the California Institute of Technology (Caltech) for constructing mass balances for pollutants which move in a connected manner through the air, land, and water of an urban-industrial region. Results are reported for lead, zinc, cadmium, and arsenic which are of special interest to the U. S. Environmental Protection Agency (EPA) and for which a reasonable amount of data were available. A balance has also been constructed for sulfur and will be described in a subsequent report. The principle on which the analysis is based is the conservation of mass for a given chemical element. Using chemical element balances in flow diagrams of the movement of pollutants through the environment, flow rates and accumulation can be estimated for the separate environmental compartments.

This method of constructing mass balances was first developed and applied to lead, zinc, cadmium, and nickel under a grant from the Rockefeller

Foundation to Caltech and published in 1975 (Huntzicker and Davidson, 1975). The mass balance for lead was more completely detailed than that of zinc and cadmium. The data for nickel were not sufficient to allow any conclusions to be made. In the Huntzicker and Davidson (1975) report, the concept of near and far deposition was introduced and the various environmental pathways through the air, land, and water of the Los Angeles area were discussed. However, little was known about the physical mechanisms of trace-metal transport in the various environmental compartments.

Advances have been made since the first mass balances report was published. The most significant gain involves new data on the physical mechanisms of trace-metal deposition. The deposition of particles containing trace metals far from the source can be predicted fairly accurately based on an understanding of these fundamentals. This method of predicting the far deposition of lead, zinc, and cadmium is described in Section III. Application of the advective diffusion equation to describe particle transport in the ocean has also been achieved, and this is covered in Section V.

Because of uncertainties in this study, the mass balance for nickel has not been included in this report. The flow of arsenic through the water pathways of the Los Angeles Basin, however, has been investigated and is presented in Section V.

SECTION II

SUMMARY

The development of a mass balance can be carried out by using a flow diagram for each species of interest. The data necessary to prepare such a diagram can be divided into three main categories: source or input data, receptor site data, and output data. The last category refers to the flow of the pollutant out of the urban area and into adjoining areas. The types of information required for each category are listed in Table 1.

TABLE 1. TYPES OF INFORMATION NECESSARY FOR DETERMINING FATE OF AIRBORNE TRACE-METAL POLLUTANTS

Source or Input Data

- Identity of sources
- Mass emission rate for each source
- Aerosol size distribution for each source

Receptor Site Data

- Deposition rate (dry)
- Rainout-washout rate

Output Data

- Atmospheric flushing (ventilaton) rates (i.e., inputs to contiguous, nonurban regions)
    - Receptor site atmospheric concentration
    - Volumetric flow through the air basin or appropriate tracer

(Continued)

TABLE 1. TYPES OF INFORMATION NECESSARY FOR DETERMINING FATE OF AIRBORNE TRACE-METAL POLLUTANTS (Continued)

- Inputs to coastal waters, lakes, rivers, etc.
    - Deposition rate (dry)
    - Rainout-washout rate
    - Runoff
    - Sewage

The primary criterion for success in an analysis of pollutant flow is that a satisfactory mass balance be obtained; that is, the sum of the input flows should equal the sum of the output flows and stored quantities. However, such an analysis is not possible without the source emission rates. The lack of such rates is the primary difficulty in this type of analysis. An inaccurate emission inventory can sometimes result in the failure to identify an important environmental pathway.

The major environmental pathways for an aerosol are by ventilation (removal from the urban area by wind) and deposition within the urban area. The ventilation rate is estimated by assuming that the air basin is a continuously stirred chemical reactor. In this approximation the ventilation rate, q_i, of species i is:

$$q_i = \overline{[i]}\ Q \tag{1}$$

where $\overline{[i]}$ is the average receptor site concentration of species i and Q is the volumetric air flow through the basin. In general, however, Q is not known, and a tracer method must be used. One such tracer for the volumetric air flow is carbon monoxide which is essentially an unreactive species. Because of its nonreactivity the input and outflows of carbon monoxide are equal. With carbon monoxide as a tracer, the following approximate relationship was used to determine q_i

$$q_i = q_{CO}\,\overline{[i]/[CO]} \tag{2}$$

[CO] is the atmospheric concentration of carbon monoxide and q_{CO} is the known input rate of carbon monoxide. This approach works particularly well when carbon monoxide and species i have a common source (e.g., Pb and CO) and less well when the sources are different.

An example of the flow of automobile-emitted lead through the Los Angeles Basin is represented in a general flow diagram for trace metals emitted by the automobile shown in Figure 1. This diagram shows the transport of a pollutant from the source and its eventual fate in the environment. Three main possibilities are indicated. Some material may become bound to the soil after deposition. Other material may deposit in local bodies of water, where it may remain in solution or suspension, or sink to the sediments. Finally, the pollutant may remain airborne and leave the urban region. The particular pathway followed, as well as the eventual fate of the material, is of great importance in terms of environmental effect and chemical speciation. In Figure 1, physical processes are designed by rectangles and receptors are represented by ellipses. Emissions from an air pollution source generally include a wide variety of particles and gases. Most of the trace metals, with which this report is concerned, are associated with the particulate component.

The greatest loss rate of particles from the atmosphere occurs nearest the source. In the case of automobile emissions, large particles, such as reentrained tailpipe material and tire dust, may deposit in relatively large quantities on or near roadways. The rate of deposition usually decreases with increasing distance from the source.

Environmental effects of near and far deposition are likely to be different. Near deposition occurs mainly on the roadway and, therefore, significant fractions of material ultimately reach sanitary landfills, as well as the coastal waters. Most of the landfill material becomes immobilized, while the trace metals reaching the coastal waters enter as point sources.

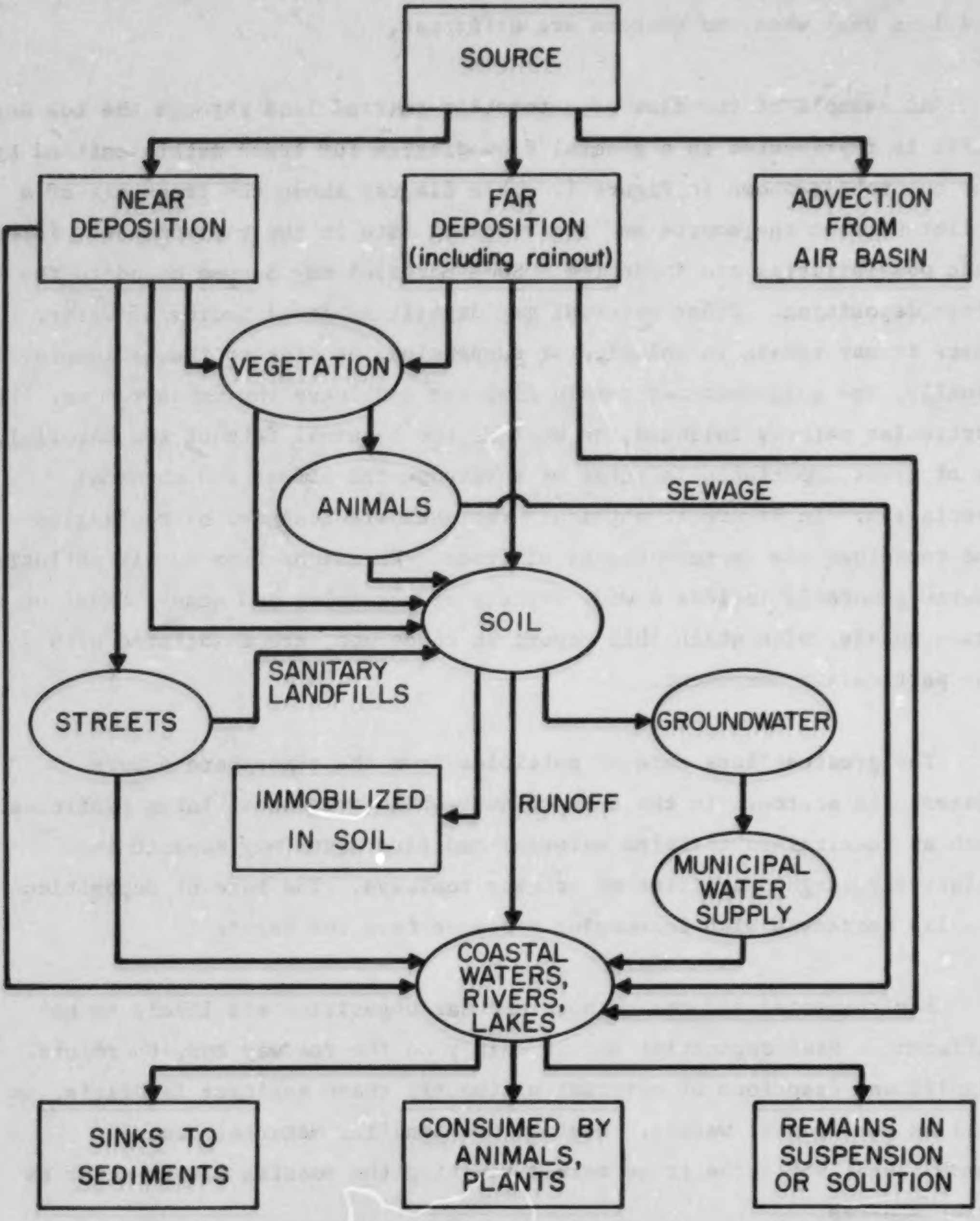
SOURCE
NEAR DEPOSITION
FAR DEPOSITION (including rainout)
ADVECTION FROM AIR BASIN
VEGETATION
ANIMALS
SEWAGE
SOIL
SANITARY LANDFILLS
STREETS
GROUNDWATER
IMMOBILIZED IN SOIL
RUNOFF
MUNICIPAL WATER SUPPLY
COASTAL WATERS, RIVERS, LAKES
SINKS TO SEDIMENTS
CONSUMED BY ANIMALS, PLANTS
REMAINS IN SUSPENSION OR SOLUTION

Figure 1. Example of a flow diagram for automobile-emitted trace metals.

On the other hand, far deposition occurs over large regions, acting as an area source rather than as a point source to the coastal waters. While near deposition involves "hot spots" of material, far deposition is more evenly spread over a large area.

Near deposition is controlled by gravitational sedimentation. Because of the short residence times of large particles in the atmosphere, meteorology has little influence on near deposition. Surface roughness is also relatively unimportant, except when the height of the roughness elements becomes large enough to cause inertial impaction.

Far deposition of trace materials has been shown by recent data to be controlled by sedimentation for smooth, flat surfaces and low windspeeds. In the case of rough surfaces and moderate windspeeds, however, it is likely that inertial impaction is important. Meteorological effects strongly influence far deposition.

Figure 1 traces the pathways followed by particles through the environment. Note that plants and animals, which may be harmed by the particles, are receptors in a number of different pathways. Near deposition may occur on streets or on the soil and vegetation. Traffic on a road located near a body of water may be a source for direct deposit on the water. However, particles are more likely to reach bodies of water by being carried off the streets via surface runoff. Street sweeping is also important since road dust is brought to sanitary landfills where it is buried in the soil. This is discussed in greater detail in Section IV.

Once particles reach the soil by either near or far deposition, there are three possible routes which may be taken. If the particles become bound to soil particles, they may become immobilized. If the particles are soluble and the soil porous, they may be carried by rainwater percolation into the groundwater system. If the particles have deposited on the surface of the soil, they may remain there until storm runoff washes them away; subsequently dissolved metals may be artificially recharged into local groundwater basins. These possibilities are discussed further in Section IV. In either of the latter two routes, the material will eventually reach a body of water. Large particles will then sink to the sediments, while smaller particles may dissolve and remain in solution. The material may be consumed by plants or animals, becoming part of the food chain before eventually dissolving in solution or sinking to the sediments.

MASS BALANCES FOR TRACE METALS: STATE-OF-THE-ART

The most complete analyses made to date have been carried out for lead in the Los Angeles Basin. The results of these analyses can be summarized in the form of a matrix equation as follows:

$$\vec{S} = [P] \vec{E} \tag{3}$$

where $\vec{S}$ = sink vector $[S_1\ S_2\ S_3\ \ldots\ S_n]$

$\vec{E}$ = source emissions vector $[E_1\ E_2\ E_3\ \ldots\ E_m]$

$[P]$ = source-to-sink matrix, $\underline{n} \times \underline{m}$

Here the elements of $\vec{S}$ and $\vec{E}$ have units of metric tons* of lead per day, while the elements of [P] are the fractions of lead emitted from each source ultimately reaching each sink. The sum of elements in the first column [P] is not unity as expected under ideal conditions since the agreement between input and output routes was not perfect.

The source and sink vectors are as follows:

S_1 = retained in vehicle

S_2 = buried in sanitary landfill

S_3 = deposited on soil, vegetation

---

* Throughout this report, the term "tons" referes to metric tons, where 1 metric ton equals 1,000 kilograms.

S_4 = remains airborne
S_5 = enters coastal waters

E_1 = vehicle emissions = 23.7
E_2 = sewage = 0.6

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \end{bmatrix} = \begin{bmatrix} 0.245 & 0.0 \\ 0.060 & 0.0 \\ 0.410 & 0.0 \\ 0.220 & 0.0 \\ 0.035 & 1.0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \end{bmatrix} \qquad \text{So, } S = \begin{bmatrix} 5.8 \\ 1.4 \\ 9.7 \\ 5.2 \\ 1.4 \end{bmatrix} \tag{4}$$

The total lend mass balance is developed and presented in Section IV. It is shown that fair agreement has been obtained between input and output quantities indicating that most of the major sources and sinks have been accounted for.

Lead is the only element, however, for which a relatively complete mass balance has been obtained. One reason for this is that an accurate source emission inventory has been used. Lead emissions can be readily estimated since there is only one major source category. Data on fuel consumption and the lead content of gasoline can be obtained, hence calculating lead emissions is relatively simple. Further the levels of lead found in the environment are well within the range of sensitivity of current analytical techniques, thus simplifying sampling and analysis and assuring that accurate data can be obtained.

Although a reasonable lead mass balance has been developed, a complete picture is not available. The eventual fate of lead buried in sanitary landfills is still unknown, as is the fate of lead carried out of the Los Angeles Basin by winds is uncertain. Also, the amount of lead removed from the atmosphere by precipitation needs further study.

The construction of a mass balance for other elements is more difficult than for lead. The major obstacle in the construction of a zinc balance is the difficulty in obtaining accurate source emissions data. Unlike lead, which is emitted from one major type of source, zinc comes from a variety of mobile and stationary sources.

Zinc emissions from mobile sources result from the abrasion of truck and automobile tires, and from combustion of detergent lubricating oils. The zinc content of tire rubber and lubrication oils has been estimated, and the zinc emissions rates have been calculated in Section IV. However, there are large uncertainties in these calculations. For example, zinc deposition measurements near a Los Angeles freeway could account for only 10 percent of the calculated tire dust zinc emissions. This suggests that tire dust deposits directly on the roadway and in areas where tire abrasion is more severe.

It is also difficult to obtain accurate estimates of zinc emissions from stationary sources. These are mainly metallurgical operations. The method of obtaining stationary source emission estimates shown in Section IV involves using data on the total mass of particulate emissions along with estimates of the zinc content of such emissions. The percentage of zinc varies greatly from plant to plant, as does the total mass of particulate emissions. Hence the zinc emissions from stationary sources as well as mobile sources can only be roughly estimated. As a result, only an approximate mass balance has been obtained for zinc. The fair agreement between input and output routes suggests that the major sources and sinks have been included in spite of the uncertainties.

A satisfactory mass balance has not been obtained for cadmium. Data compiled in Section IV show that the outputs greatly exceed the inputs. This suggests that all of the sources of cadmium have not been accounted for and it is likely that both the mobile and the stationary source emissions estimates are low. For example, measurements of cadmium could account for only 70 percent of the calculated tire dust cadmium emissions. Stationary source cadmium emissions are likewise difficult to estimate. There are a number of metallurgical operations and cadmium chemical plants in the area, but little data are available on emissions from these sources.

In addition to difficulties in obtaining source data, the levels of cadmium present in the Los Angeles area are very low. Analyses are difficult, and background levels are high. More research is needed to obtain a reasonable mass balance for cadmium.

Very little data on arsenic are available, and hence no mass balance was constructed. However, it is likely that there may be no major sources of atmospheric arsenic in the Los Angeles area. Phosphate plants in the Los Angeles Basin may be a source of certain trace metals such as zinc, cadmium, and arsenic but emissions from these phosphate plants were not considered in the present study. Thus, only the water route for arsenic was examined and this is discussed in Section V.

In summary, fair agreement between input and output masses has been obtained for a few elements using the guidelines set up in this report. It should be possible to gather sufficient data to construct mass balances for additional elements of public health and ecological interest by this method. Obtaining accurate source emissions data, identifying environmental pathways and sinks, and determining the source-to-sink relationships are the keys to constructing accurate balances. Insufficient data exist for some toxic elements of interest and research in these areas should be encouraged.

MASS BALANCES FOR TRACE METALS: FUTURE PROSPECTS

In the previous discussion it has been assumed that the Los Angeles Basin is a continuously stirred chemical reactor because it is a relatively isolated meteorological area in which reactions are occurring. Future mass balance studies are likely to be based on more detailed methods permitting concentration estimates of more widely dispersed agents of interest.

For example, from a fundamental point of view, the transport and fate of particulate matter emitted by the automobile or found in stack plumes can be estimated by making use of the General Dynamic Equation (GDE) for determining aerosol behavior (Friedlander, 1976). This equation takes into account particle formation, growth, diffusion, coagulation, deposition, and advection by the winds. The GDE for an external force field is shown as equation 5. Here n(v) is the number distribution function defined for all particle volumes v, and $\int_0^\infty n(v)\,dv = N$, the total number concentration of particles in all size ranges.

$$\frac{\partial n}{\partial t} + \nabla\cdot n\vec{v} + \frac{\partial ns}{\partial v} = \nabla\cdot D\nabla n + \frac{1}{2}\int_0^v \beta\,(\tilde{v}, v-\tilde{v})n(\tilde{v})n(v-\tilde{v})\,d\tilde{v}$$
$$-\int_0^\infty \beta\,(v,\tilde{v})n(\tilde{v})n(v)d\tilde{v} - \nabla\cdot\vec{c}n \qquad (5)$$

t = time

$\vec{v}$ = velocity of the fluid suspending the particle

D = Brownian diffusion coefficient

$\vec{c}$ = particle velocity relative to fluid due to an external force field

s = particle growth law dv/dt

The first term $\frac{\partial n}{\partial t}$ represents the time rate of change of the function n due to the various mechanisms. This term must be nonzero unless the system is in a steady state.

The second term $\nabla\cdot n\vec{v}$ represents advection of particles, for example, by wind. For the usual case of incompressible flow, $\nabla\cdot\vec{v}$ is zero and this term becomes $\vec{v}\cdot\nabla n$.

The third term takes particle growth into account. Growth here refers to any gas-to-particle conversion process.

On the right hand side $\nabla\cdot D\nabla n$ represents Brownian diffusional transport. Since in general D is not a function of position, this term becomes $D\nabla^2 n$.

The second term on the right hand side describes the formation rate of particles of size v due to the collision of smaller particles of size $v-\tilde{v}$ and $\tilde{v}$. The term following also represents coagulation which in this case is the loss rate of particles of size v with all other sizes.

Finally, the last term on the right hand side represents particle motion in the influence of an external force field. In the case of gravitational sedimentation, $\nabla\cdot\vec{c}n$ merely becomes $v_s \frac{\partial n}{\partial z}$, where v_s is the settling velocity which is taken to be negative in the -z direction.

For the atmosphere, a form of the GDE for turbulent conditions must be used. It is assumed that the fluid velocity v, the number distribution function n, and the particle growth law s can be written as the sum of the mean and fluctuating components:

$$\begin{aligned} \vec{v} &= \bar{\vec{v}} + \vec{v}' \\ n &= \bar{n} + n' \\ s &= \bar{s} + s' \end{aligned} \tag{6}$$

Substituting these relations into equation 5 and averaging with respect to time yields the following result for steady turbulent flow:

$$\begin{aligned} \bar{\vec{v}}\cdot\nabla\bar{n} + \overline{\frac{\partial ns}{\partial v}} + \overline{\frac{\partial n's'}{\partial v}} = &- \nabla\cdot\overline{n\vec{v}'} + D\nabla^2\bar{n} + \frac{1}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v})\bar{n}(\tilde{v})\bar{n}(v-\tilde{v})d\tilde{v} \\ &- \int_0^{\infty} \beta(v,\tilde{v})\bar{n}(v)\bar{n}(\tilde{v})d\tilde{v} + \frac{1}{2}\int_0^v \beta(\tilde{v},v-\tilde{v})\overline{n'(\tilde{v})n'(v-\tilde{v})}d\tilde{v} \\ &- \int_0^{\infty} \beta(v,\tilde{v})\overline{n'(v)m'(\tilde{v})}d\tilde{v} - v_s \frac{\partial\bar{n}}{\partial z} \end{aligned} \tag{7}$$

The third term on the left hand side is the fluctuating growth term which depends on the correlation between n' and the local concentration of gaseous species converted to particulate matter. The first term on the right hand side represents the change in $\bar{n}$ resulting from turbulent diffusion; the individual components of the vector flux $\overline{n'\vec{v}'}$ are usually assumed to follow an equation of the form:

$$\overline{n'v'}_i = -\varepsilon_i \frac{\partial \bar{n}}{\partial x_i} \tag{8}$$

where the eddy diffusivity ε_i is a function of position. The fifth and sixth terms on the right hand side are the contributions to coagulation resulting from the fluctuating concentrations.

Although the GDE has not yet been used to construct mass balances, studies related to this equation have been conducted for future mass balance calculations. Studies discussed in Section III on the physical mechanisms of far deposition for lead, zinc, and cadmium in the Los Angeles Basin involve the determination of the deposition velocities of these species. Such data will be of value in the development of deposition models based on the GDE. Numerical solutions to the advective diffusion equation applied to sewage particles in the ocean are examined in Section V. This form of the GDE may have direct application to mass balances but this work has not yet been conducted.

SECTION III

RELATION BETWEEN AIRBORNE CONCENTRATION AND DEPOSITION OF TRACE METALS

The deposition of trace metals is expected to decrease with distance from the source, i.e., a roadway. Most of the decrease occurs within about 100 meters from the road; at greater distances the deposition is essentially independent of distance and is termed "far deposition." The "near deposition" region has been defined as the distance over which the deposition rate falls to within 10 percent of the far deposition rate.

It is understood that the far deposition rate may vary in different parts of an urban area. Thus the size of the near and far deposition regions as well as the actual deposition rates may also vary within the area.

Although the general dynamic equation cannot be solved for most cases involving atmospheric transport, there are a few situations where the basic theory may be directly applied. One such case is the deposition of certain particles containing trace metals on smooth, flat surfaces. The deposition of particles containing lead, zinc, and cadmium on surfaces such as smooth soil, roadways, and other flat areas may be directly predicted under certain conditions. In particular, these predictions may be made when there is sufficient mass in large particulates so that gravitational sedimentation is important, and when the windspeed is not so excessively high that turbulent deposition dominates.

Airborne concentrations of trace metals in urban areas have been measured by several investigators, and it is generally known that urban air contains significantly higher trace metal levels than air from nonurban regions. Lee and von Lehmden (1973) have shown that urban activities such as fuel combustion contribute a major portion of the trace metals emitted into the atmosphere. Their data show concentrations of iron, lead, magnesium, and zinc in excess of 1 microgram per cubic meter ($\mu g/m^3$) in many cities. Lazrus et al. (1970) have examined trace metals in precipitation throughout the United States and have found considerably greater concentrations near population centers. For example, they found the lead content of rainwater to be correlated with gasoline consumption in a given area.

Airborne concentrations of lead have been measured near roadways by many investigators (Bullock and Lewis, 1968; Cahill and Feeney, 1973; Daines et al., 1970; Rolfe and Haney, 1975). Studies by Cardina (1974) and Pierson and Brachaczek (1974) have shown that particles of rubber tires can be identified in the dust collected near roadways. This dust contains significant amounts of zinc which contributes to the total airborne zinc concentration in urban areas. Metallurgical emissions also contribute to urban levels of zinc and other trace metals.

A knowledge of deposition rates for these trace metal particles has many applications. Information on particle residence time in the atmosphere can be obtained from deposition studies. The effects of sources on downwind regions are linked to deposition rates. Deposition rates are also useful when setting up tracer studies.

Most trace-metal deposition studies have focused on lead-containing particles. Rabinowitz (1972) has measured the lead content of wild oat grass (*Avena sativa*) in urban and nonurban areas of Southern California. The lead associated with these plants was shown to be deposited airborne material rather than internally incorporated material from the soil. Patterson and Settle (1974), Huntzicker et al (1975a), and Davidson et al. (1974) have examined the deposition of lead on flat Teflon plates which were placed in cities as well as in the mountain, desert, and coastal areas of

Southern California. Similar studies involving the lead deposition on artificial surfaces have been conducted by Atkins (1969) in Palo Alto and by Servant (1974) in France. The results of several lead deposition studies are summarized in a report by Chamberlain (1974).

The specific case of automobile-emitted lead depositing on soil and vegetation near roadways has been examined by several investigators. Kloke and Riebartsch (1964) have measured a high lead content in grass growing near busy streets. Heichel and Hankin (1972) have detected large lead particles deposited on trees near a roadway. The lead content of soil near a highway was compared with lead in soil samples obtained near a battery smelter and from a greenhouse soil supply (Marten and Hammond, 1966). Rapid decreases in the lead content of vegetation with increasing distance from highways have been measured by several experimenters (Rolfe and Haney, 1975; Cannon and Bowles, 1962; Cholak et al., 1968; Chow, 1970a; Page et al., 1971). Other researchers have examined several varieties of plants with high lead contents growing near roads, investigating whether the lead is deposited airborne material or translocated from the soil (Dedolph et al., 1970; Leh, 1966; Motto et al., 1970; Schuck and Locke, 1970; Ter Haar, 1970; Rabinowitz, 1972).

The deposition of other trace metals has also been examined. Peirson et al. (1973) have studied the deposition of several elements in England. Lagerwerff and Specht (1970) have measured the lead, zinc, nickel, and cadmium content of soil and grass at various distances from roadways in Eastern and Midwestern United States. They found a decrease in metal content with increasing distance from the road. Similar gradients have also been measured by Huntzicker and Davidson (1975) near a Los Angeles freeway. In other studies, Huntzicker et al. (1974) have measured the deposition of zinc, nickel, and cadmium on flat Teflon plates in Southern California.

Although there is a wealth of trace-metal data available, little research has been done to investigate the deposition mechanisms involved. Several investigators have measured the deposition of monodispersed particles in the laboratory and under controlled field conditions, but these results have not previously been applied to ambient trace-metal deposition.

The work discussed in this report involves experimental determination of airborne size distributions of particles containing lead, zinc, and cadmium in Pasadena. The distributions are then used to calculate deposition on a flat surface. The calculated values are compared with experimental deposition data obtained simultaneously with the size-distribution measurements. It is expected that these calculated and measured depositions for smooth, flat surfaces will be the lower limits of the actual deposition on rough, natural surfaces.

All particle diameters refer to aerodynamic equivalent diameters, unless otherwise noted. A particle with an aerodynamic equivalent diameter (dp), regardless of shape or density, will have the same inertial properties as a unit-density sphere of diameter dp. The value of dp in a size-distribution of particles where 50 percent of the total mass is greater and 50 percent smaller than this diameter is defined as the mass median equivalent diameter (MMED). The geometric diameter is the actual distance across the particle; it is thus difficult to apply this concept to an irregularly shaped particle.

THEORY OF DEPOSITION

It is convenient to begin by defining the deposition velocity v_g:

$$v_g = -\frac{J}{C} \qquad (9)$$

where v_g has units of centimeters per second (cm/sec), J is the flux of material to a surface in nanograms per square centimeters per second ($ng/cm^2/sec$), and C is the airborne concentration in nanograms per cubic centimeter (ng/cm^3). The flux is assumed to be constant with height above the surface, although C and v_g are functions of height.

The relationship between flux and concentration can be written:

$$J = (D+\varepsilon)\frac{dC}{dz} - v_s C \qquad (10)$$

where D and ε are the Brownian and eddy diffusivities, respectively, in square centimeters per second (cm^2/sec), z is the height above the surface in cm, and v_s is the sedimentation velocity in cm/sec. The sedimentation velocity of a particle is reached when the aerodynamic drag force on a falling particle exactly balances the gravitational force. The minus signs are necessary since the flux downward to a surface is a negative quantity by convention and the deposition velocity is defined as positive.

Equation 10 applies to both small and large particles. For very small particles, the sedimentation term is negligible. It is also assumed that D is very much less than ε, except very close to the surface or when there is no wind. Thus for small particles, introducing the relationship $\varepsilon = ku^*z$, equation 10 reduces to:

$$J = -\varepsilon\frac{dC}{dz} = -ku^*z\frac{dC}{dz} = -ku^*\frac{dC}{d(\ln z)} \qquad (11)$$

where k is von Karman's constant equal to 0.4, u* is the friction velocity in cm/sec, and ln z is the natural logarithm of height.

For large particles, the diffusivities are negligible so equation 10 becomes:

$$J = -v_s C \qquad (12)$$

Comparing equations 9 and 12 shows that the deposition velocity equals the sedimentation velocity for large particles.

Equation 11 may be used to calculate the deposition of small particles when dC/d(ln z) is known. For example, Figure 2 shows a plot of condensation nuclei concentration versus height over a field of wild oat grass in residential Los Angeles. The value of C(4 meters) is 45,000 particles per cubic centimeter. Two condensation nuclei counters (CNC) were used to make these measurements (General Electric CNC, and Environment One Model Rich 100). A hot wire anemometer was used to determine u*. When plotted on a logarithmic scale of height, as in Figure 3, a value of dC/d(ln z) is obtained which may be substituted into equation 11. The resulting calculated flux for these experiments is -40,000 particles/cm^2/sec. The deposition velocity from equation 9 is thus 0.9 cm/sec at a height of 4 meters.

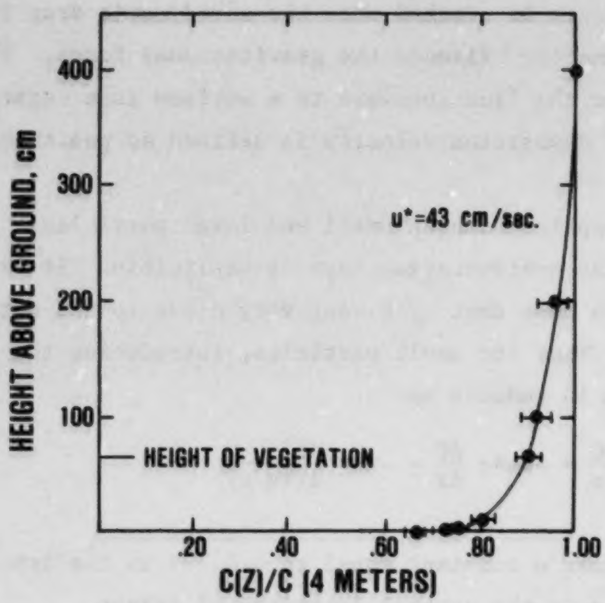

Figure 2. Airborne concentrations of condensation nuclei as a function of height.

The linear relationship shown in Figure 3 implies that the condensation nuclei were approximately monodisperse. If the nuclei size-distribution were polydisperse, the different-sized particles would have correspondingly different fluxes, hence different dC/d(ln z) values. Therefore the overall effective dC/d(ln z) would probably vary with height.

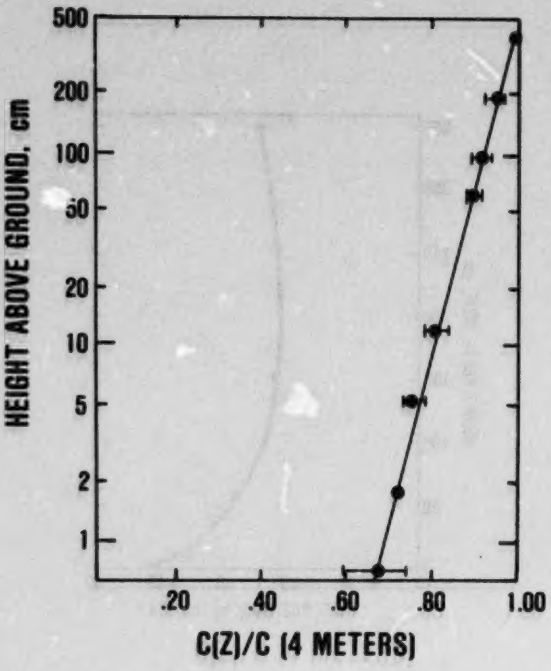

Figure 3. Data from Figure 2 plotted on a logarithmic scale.

In the case of large particles, a different concentration profile is expected. Figure 4 shows a plot of lead mass-deposition on flat Teflon plates. The plates were located at several heights above the roof of the W. M. Keck Laboratories at Caltech about 15 meters above the ground. If the lead particles depositing on each plate are from the same portion of the airborne size-distribution, then the deposited mass is proportional to the airborne concentration of lead in that size range.

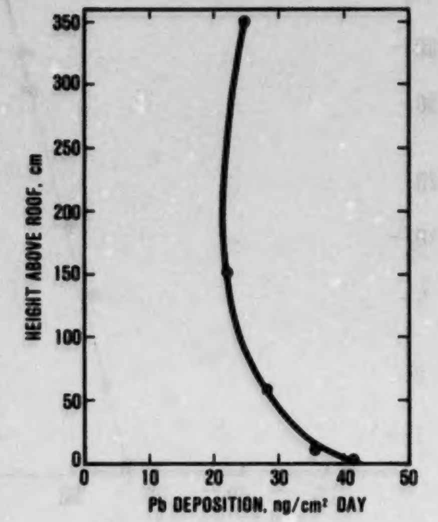

Figure 4. Total deposition of lead on Teflon plates at various heights.

At heights above 1 meter, the deposition is roughly constant with height. Below this height, the deposition increases, indicating a source of lead particles on the roof surface. This is probably due to resuspension of roof dust by wind eddies. This premise is supported by a measurement of high lead content in the roof dust in a subsequent experiment.

It should be mentioned that although equation 10 simplifies to equation 11 or 12 for small or large particles, the general case has been examined by other researchers. For example, equation 10 has been integrated by Chamberlain (1966) and shown in greater detail by Sehmel (1970), based on special assumptions concerning the form of a ε near the surface.

It will be shown that equation 12 is applicable for certain trace metals at the CalTech site because there is sufficient mass in large particles to control deposition by sedimentation.

SIZE-DISTRIBUTIONS

Many investigators have measured lead size-distributions at the source, the automobile tailpipe. Hirschler et al. (1957, 1964) used an electrostatic precipitator to collect auto exhaust particles. They then washed the particles into a solution and fractionated them by repeated centrifugal sedimentations. The results of their experiments showed that particles containing lead in auto exhaust covered a wide spectrum of sizes, from 0.01 micrometers (μm) to several millimeters in diameter. For city-type driving, one-third to one-half of the lead was in particles greater than 5 μm in geometric diameter (12.2 μm aerodynamic equivalent diameter) assuming that lead bromochloride (PbBrCl) has a density of about 6 grams per cubic centimeter (g/cm^3). Ninomiya et al. (1971) measured the sizes of particles containing lead in diluted auto exhaust with vehicles operating under the 7-mode cycle of the Federal Test Procedure (Federal Register No. 108, 1968). Their results showed 20 to 30 percent of the exhausted lead particles were of 500 to 5,000 μm in geometric diameter and were expelled in the first few cycles after a cold start. Ter Haar et al. (1972) has used the Federal Test Procedure and has collected auto exhaust in a large black polyethylene bag. Sizing these particles showed that 55 percent of the lead mass exhausted was associated with particles greater than 5 μm in equivalent diameter. It is interesting to note that Ter Haar found a mass median equivalent diameter (MMED) of only 0.5 μm when the vehicle was operated under steady cruising conditions rather than the Federal cycle. Habibi (1973) has reported that 57 percent of the particles containing lead in auto exhaust are greater than 9 μm equivalent diameter, for a car with 28,000 miles (45,000 km). His vehicles were operated under the Federal Mileage Accumulation Schedule (Federal Register No. 2, 1968).

Two investigators have conducted similar tailpipe studies but have not seen significant lead in large particles. Mueller et al. (1964) found 62 to 80 percent of the lead mass in particles smaller than 2 μm in equivalent diameter. His studies involved automobiles operated under steady cruising conditions, and the results are consistent with Ter Haar's lead MMED of 0.5 μm for steady cruising. Lee et al. (1971) operated an automobile according to a 5-minute cycle similar to the California cycle. The exhaust was sampled from animal inhalation exposure chambers. These studies showed that 95 percent of the lead mass was in particles smaller than 0.5 μm in equivalent diameter.

Difficulties in performing these tailpipe experiments as well as variations in automobiles, fuel, and driving cycles account for the differences among the results of the above investigators. Habibi (1973) discusses some of these difficulties. In general, however, the results indicate that relatively new, steadily crusing automobiles emit predominately submicron lead. Older autos and rapidly accelerating or decelerating autos emit both micron and submiron lead particles. It is therefore likely that ambient urban atmospheres which receive emissions from wide varieties of vehicles and driving patterns contain a broad spectrum of sizes of particles containing lead.

The situation for particles containing zinc and cadmium has also been investigated. Metallurgical emissions and automobiles (tire dust) are the major sources of zinc. The metallurgical emissions are generally submicron while the tire dust is larger. It is therefore likely that much of the zinc deposited in urban areas, especially near roadways, is from tire dust.

Cardina (1974) has measured the size distribution of road dust a few meters from an urban freeway. He found one-third of the total mass in particles larger than 7 μm in equivalent diameter. These large particles had a high mass fraction of rubber, presumably from tire dust, and would therefore contain a significant amount of zinc.

Pierson and Brachaczek (1974) have measured both airborne and settled highway dust. Their data show that most of the lead and zinc deposited near roadways are large particles (50 to 500 μm in geometric diameter), and that most of the tire dust is found in large, nearly nonsuspendible particles of which only a small fraction becomes airborne. Dannis (1974b) has examined tire dust collected on plates mounted underneath a car. His findings show a MMED for rubber of about 20 μm, with very few rubber particles smaller than 3 μm in equivalent diameter.

These investigations indicate that ambient particles containing lead should be widely distributed over a large range of sizes. The ambient zinc distribution should be bimodal: a submicron peak from combustion and metallurgical emissions, and a supermicron peak from tire dust. The ambient cadmium distribution may resemble the zinc spectrum. Substances which contain zinc generally contain trace amounts of cadmium because the two elements are found together in nature (Friberg et al., 1974). In some regions, additional sources of cadmium may be present.

Measurements of ambient trace-metal size-distributions have been concerned with the respirable range near and below one micron. These studies were generally nonisokinetic and therefore underestimated the amount of material in large particles. Watson (1954) has shown that sampling with an air inlet oriented 90° to the wind, such as an upright impactor, results in collecting less than 45 percent of the 12 μm particles and less than 10 percent of the 37 μm particles present (equivalent diameters).

Tufts (1959) measured sizes of particles containing lead using a chemical microscopic spot test, sizing red dots of precipitate. The results for ambient air near heavily traveled streets showed the bulk of the lead in particles between 0.1 and 2.7 μm in geometric diameter. There was lead detected in particles as large as 13.4 μm. Lininger et al. (1966) measured airborne lead near a busy street and found large variations in the size-distributions among runs. Robinson and Ludwig (1967) used a modified Goetz spectrometer (Goetz et al., 1967) to obtain size-distributions of lead in remote and urban areas throughout the United States. Surprisingly, little variation in the shapes of the distributions was found, with the average MMED being 0.25 μm. Cholak et al. (1968) measured lead size-distributions 10, 400, and 3,400 meters from a busy interstate highway with Andersen impactors. About 70 percent of the lead mass was found in particles smaller than 1 μm in equivalent diameter. The extrapolated MMED was about 0.3 μm. Negligible differences appeared among the distributions from the three sites. Daines et al. (1970) used cascade impactors located 10, 75, and 500 meters from the highway. They found 65 percent of the lead mass in particles smaller than 2 μm, and 85 percent less than 4 μm in geometric diameter with little difference in the spectra at the three sites. Lundgren (1970) measured lead size-distributions in an urban area with a Lundgren impactor and found an MMED of 0.5 μm with 5 percent of the mass in particles greater than 17 μm in equivalent diameter.

Some investigators have examined zinc and cadmium as well as lead distributions. Harrison et al. (1971) used a modified Andersen impactor to sample lead and cadmium in an urban atmosphere. They found 60 percent of the lead mass on the afterfilter (<0.2 μm in equivalent diameter) in a unimodal distribution, while cadmium was characterized by a bimodal distribution with very little material on the afterfilter. Lee et al. (1968, 1971) conducted several studies measuring distributions of lead, zinc, and cadmium in urban areas. Their results showed 68 percent of the lead, 40 percent of the zinc, and 28 percent of the cadmium in particles smaller than 1 μm in equivalent diameter. Lee and von Lehmden (1973) also summarized the MMED from several researchers and found that lead has consistently smaller MMED values than either zinc or cadmium. In particular, the lead MMED range from 0.2 to 1.43 μm, zinc from 0.58 to 1.79 μm, and cadmium from 1.54 to 3.1 μm. In more recent studies, however, Lee and Goranson (1975) have measured an increasing trend in total particulate mass MMED for the period 1970-1972.

To summarize the results of the above survey, it is apparent that airborne lead is mainly found in submicron particles with about one-third of the mass being supermicron. However, zinc and cadmium have greater fractions in the supermicron range.

ATMOSPHERIC SIZE-DISTRIBUTIONS: ISOKINETIC EXPERIMENTS

Isokinetic impactor runs were conducted using a modified Andersen model 20-000 sampler. The modifications involved construction of a new orifice and two top stages for better fractionation of large particles. Stickey Teflon Temp-R-Tape (Connecticut Hard Rubber Company) was used as an impactor substrate. It was found that the adhesive and the particles completely dissolved in a hot solution of 1 part concentrated hydrofluoric acid and 20 parts concentrated nitric acid. After evaporation and redissolving, the resulting solution was analyzed for lead and zinc with flame atomic absorption spectroscopy, and for cadmium with flameless atomic absorption (carbon rod atomization).

Measurements were made on the roof of W. M. Keck Laboratories at Caltech which is more than 300 meters from the nearest heavily traveled street, but less than 1 kilometer from several such streets. The impactor was positioned horizontally facing into the wind, 150 cm above the roof surface. At this height, resuspended roof dust was not a problem. The wind direction was checked frequently during the runs, and if the direction was found to have changed by more than 20°, the impactor direction was also changed. It was found that the wind direction changed little during the experiments, although short gusts of wind varying $\pm 45^{\circ}$ occurred occasionally. A flow rate of 13.2 liters per minute was used because at this flow the orifice airspeed was approximately equal to the average windspeed.

The first isokinetic experiment took place during May 13-15 and May 17-18, 1975. Sampling was from 8 a.m. to 8 p.m. daily. For this run, the standard eight-stage Andersen impactor was used with a modified orifice, but without modified stages. A Millipore HAWP 04700, 0.45-µm pore-size filter was used as the after filter.

The second experiment occurred from July 16-20, 1975, with the same daily sampling times as above. Two specially constructed stages were substituted for the regular Andersen stage 0 to fractionate larger particles. These new stages were similar in construction to the regular units. The uppermost stage (stage "A") had 222 jets of 1/8-inch (3.17-millimeter) diameter, while stage "B" had 110 jets of the same diameter.

Approximate values of median aerodynamic equivalent diameter (dp_{50}) for stages 3 through 6 were determined experimentally with monodisperse polystyrene latex and polyvinyltoluene particles (Dow Chemical Company). The results at 13.2 liters per minute agreed with the specifications when adjusted for the flow rate difference.

Based on effective mass mean diameters, a comparison between isokinetic runs and previous nonisokinetic runs at the same site is shown in Table 2. The data show that the fractions of particles greater than 10 µm aerodynamic diameter collected by the impactor are greater during the isokinetic runs. This shows the importance of isokinetic sampling.

TABLE 2. PERCENTAGE OF MASS GREATER THAN 10 µm AERODYNAMIC DIAMETER FOR NONISOKINETIC AND ISOKINETIC RUNS

	Pb(%)	Zn(%)	Cd(%)
November 1972*	5	11	
February 1974*	11	15	--
May 1975**	17	38	28
July 1975**	17	32	37

* nonisokinetic (Huntzicker et al., 1975a).

** isokinetic

Part of the difference between runs may be due to the 1- to 3-year period between isokinetic and nonisokinetic experiments. As Lee and Goranson (1975) have shown, the total mass distribution has been shifting toward larger particle sizes. The seasonal differences between runs may also be significant.

There is a question whether particles as large as 20 or 30 µm in equivalent diameter can remain airborne for appreciable periods of time. Lundgren and Paulus (1973) have measured total mass size-distributions in a suburban area with no strong local sources, and found a bimodal distribution with the upper mode covering 5 to 100 µm. In another study, Lundgren and Paulus (1974) examined the size-distribution of particles deposited on a fallout collector plate. They found that 90 percent of the deposited mass was associated with particles in the range of 25 to 120 µm. They also estimated that the distance which large particles normally travel varies from several meters to several kilometers from their source. A study involving the transport of lead aerosols was conducted by Gillette and Winchester (1970) in which lead size-distributions were measured at a site over Lake Michigan, far from sources, and also in Chicago. Results showed that there were only slight decreases in the fraction of lead greater than 9 µm when comparing measurements of lead in Lake Michigan with measurements in Chicago. This shows that large particles containing lead may remain airborne for at least 6 hours, the minimum transport time between the two sites. Additional evidence of large airborne lead particles has been shown by Tufts (1959) and Lundgren (1970).

Normalized distributions for lead, zinc, and cadmium based on equivalent diameters are shown in Figure 5 for the July 1975 experiment. The airborne mass concentration is indicated by ΔC which C_T represents the sum of the ΔC's from all size ranges for each trace metal. Results for the May 1975 run are in close agreement and therefore not shown. The total airborne concentrations of lead, zinc, and cadmium were 1.25, 0.13, and 0.0041 micrograms per cubic meter ($\mu g/m^3$), respectively. A total filter run in parallel with the impactor and afterfilter assembly yielded 1.11, 0.13, and 0.0036 $\mu g/m^3$.

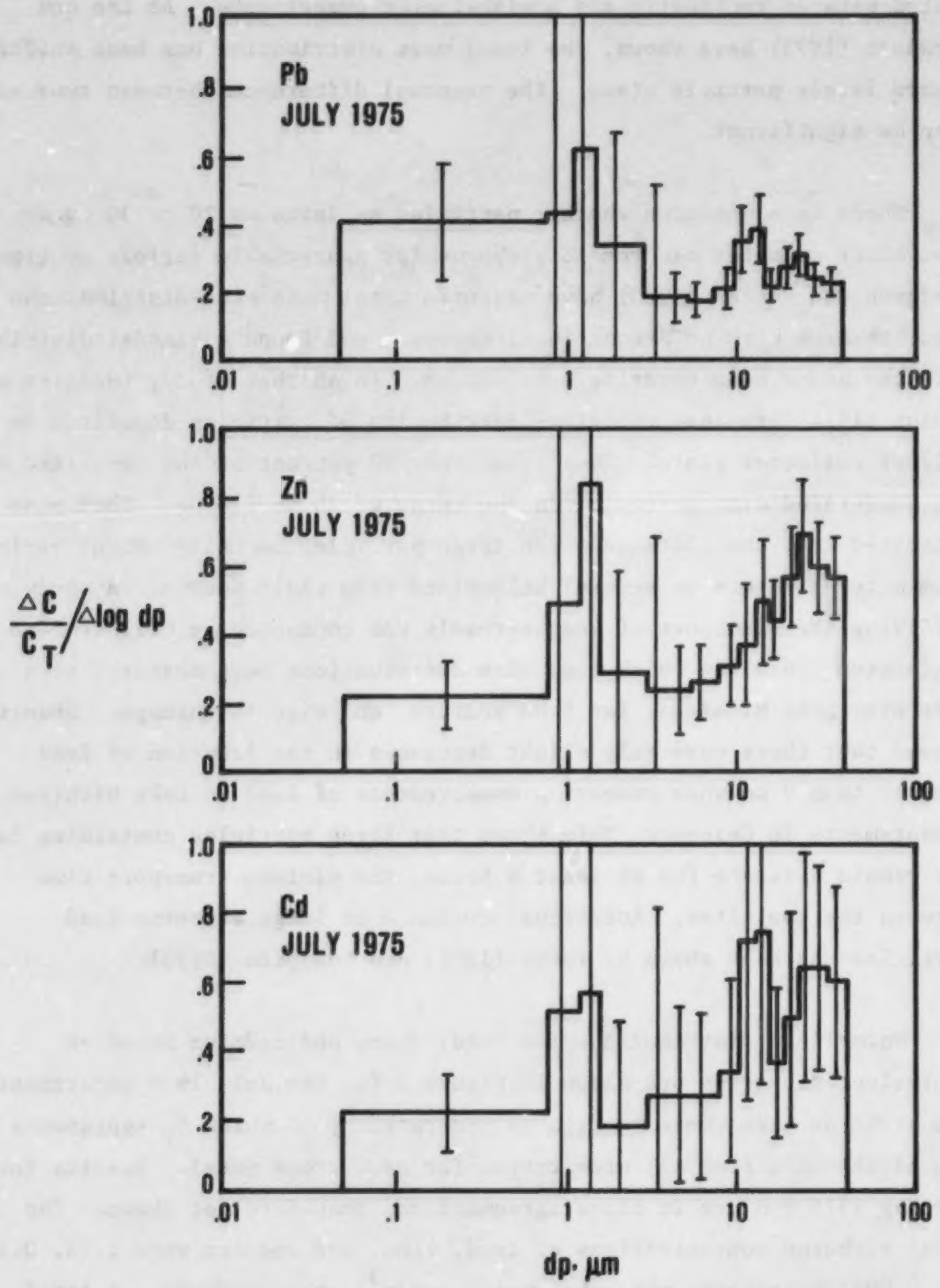

Figure 5. Normalized size-distributions for lead, zinc, and cadmium based on aerodynamic equivalent diameters.

Since the impactor was positioned horizontally, large particles settled to the walls of the instrument. The losses were calculated to be 4 percent to 11 percent of the material on the top stages; consequently, the measured upper stage masses were increased by these loss fractions. It should be noted that values of dp_{50} were not used for the stage cutoff diameters. Instead, the calibration results of Flesch et al. (1967) were used for stages 2 through 7. Stages A, B, and 1 were calibrated by running the impactor isokinetically at the same site as the trace-metal experiments, a few weeks later. Atmospheric particles were sized geometrically under an optical microscope. Basing determinations on photographs by McCrone and Delly (1973), many of the particles were observed to be spores, insect parts, and other organic material. A density of 1 g/cm^3 was assumed based on experiments by Lundgren and Paulus (1974) who measured a density of 1.1 g/cm^3 for similar particles.

Once the total mass-distributions on stages A, B, and 1 were obtained, it was assumed that the mass of trace metals collected by each of these stages had the same aerodynamic equivalent distribution as the total atmospheric mass on each stage. The distributions on stages A, B, and 1 were then summed and added to the distribution from stages 2 through 7 and the afterfilter.

A lower cutoff of 0.05 μm equivalent diameter was assumed based on the work of Hidy (1973). There were very few particles with geometric diameters greater than 40 μm, statistically too few to be significant, so the upper cutoff was determined to be 40 μm.

The error bars in Figure 5 represent one standard deviation from the mean based on analytical and measurement errors, uncertainties in the minimum and maximum diameters, and selected sampling errors. Although uncertainties in the diameters are significant when the dp is less than 4 μm, only "vertical" error bars are shown.

Figure 5 shows that lead is weakly bimodal and more uniformly distributed than either zinc or cadmium. The latter metals have strong modes above 10 µm; these findings are in agreement with the tire dust studies. Large peaks at about 1 µm for all three metals are somewhat misleading. Because of the nonideal shapes of the impactor efficiency curves, the actual peak may occur at a smaller diameter; the reasons for this are discussed at the end of this Section.

DEPOSITION OF LEAD, ZINC, AND CADMIUM

Several measurements of deposition velocities of lead in urban and rural areas have been made. In addition, a number of investigators have published values of flux J and airborne concentration C from which it is possible to calculate the deposition velocity (v_g) (equation 9). Chamberlain (1974) has summarized the results of several investigations. These and other data are presented in Table 3. All values are for dry deposition, except the data of Cholak et al. (1968) and Chow (1970b). Note that the data of Servant are for an inverted surface, and do not include the sedimentation component (Servant, 1975).

TABLE 3. DEPOSITION VELOCITIES OF LEAD

Location	Deposition Surface	v_g (cm/sec)	Investigator
Wilderness area, Northern California	Teflon plate	0.07	Patterson and Elias (1975)
San Nicolas Island	Filter paper	0.093	Peirson (1973)
Residential Toulouse, France	Deposit gauge, Inverted	0.13	Servant (1974)
Lake Windermere, Rural England	Filter paper	<0.18	Pierson et al. (1973)
Other rural sites in Great Britain	Filter paper	0.157-0.625	Pierson (1973)
15 meters from a freeway, Palo Alto, California	Polyethylene pan, 6 in. deep	0.185	Atkins (1969)

(Continued)

TABLE 3. DEPOSITION VELOCITIES OF LEAD (Continued)

Location	Deposition Surface	v_g (cm/sec)	Investigator
10 meters from a freeway, Cincinnati, Ohio	Deposit gauge, measuring both wet and dry deposition	0.475	Cholak et al. (1968)
400 meters from a freeway in a park removed from traffic, Cincinnati, Ohio	"	0.243	"
3400 meters from a freeway, in an "average residential area," Cincinnati, Ohio	"	0.370	"
Downtown San Diego	"	0.498	Chow (1970b)
La Jolla, suburban San Diego	"	0.191	"
On the shoulder of a freeway, Los Angeles	Teflon plate	1.80	Huntzicker and Davidson (1975)
Pasadena	"	0.29	present study

The data of Table 3 are best understood by considering a lead particle source emitting a known size-distribution. As this lead is transported away from the source, depositional loss to the ground as well as other processes will affect the shape of the distribution. Large lead particles with high deposition velocities will be lost first. Consequently, a smaller deposition velocity would be expected far from the source. (It is assumed that particle growth is unimportant in the size range of interest). This trend may be observed in Table 3. The highest deposition velocity, 1.8 centimeters per second (cm/sec) has been measured closest to the source, and the smallest value, 0.07 cm/sec has been measured in a remote area. The value of 1.8 cm/sec may be an upper limit due to nonisokinetic sampling.

The value of 0.29 cm/sec for Pasadena was obtained by dividing the measured lead flux onto a flat Teflon plate by the total airborne lead concentration measured by the impactor and afterfilter. It should be possible to calculate this flux, and also zinc and cadmium fluxes, using the size-distributions of Figure 5 and proper deposition velocities for each size range.

Many researchers (Chamberlain, 1966; Islitzer and Dumbauld, 1963; Sehmel, 1972; Sehmel et al., 1973) have shown that deposition velocities over rough surfaces are generally greater than sedimentation velocities for similarly sized particles. This effect is especially evident at high windspeeds. Impaction, turbulent deposition, and eddy diffusional deposition on the roughness elements are responsible for the high deposition rate when compared to sedimentation.

For a relatively smooth surface, however, Sehmel (1973) has shown that sedimentation may be controlling. In particular, v_g is shown to be equal to sedimentation velocity (v_s) for a windspeed of 2.2 meters per second (m/sec) for particles larger than 0.3 μm in equivalent diameter. A smooth brass surface was used for his study.

Three experimental surfaces were set up on the roof of Keck Laboratories to determine if slight changes in surface roughness affected lead deposition. It was found that lead fluxes to a flat Teflon plate, a fine sand surface (∿0.38 mm grains), and a coarse sand surface (∿0.64 mm grains) differed by less than 15 percent. On the basis of these results and Sehmel's findings, it was decided that sedimentation velocities can be used in an estimated calculation of trace-metal deposition on a flat Teflon plate.

The deposition flux can be calculated from mass concentration distributions for particles of a given size. The fluxes calculated from data presented in Figure 5 are listed in Table 4. The fluxes may be compared with the measured deposition on the flat Teflon plates exposed simultaneously with the July 1975 impactor run. The experimental fluxes given represent average values for sticky and nonsticky Teflon surfaces.

Fluxes calculated from the May 1975 impactor experiment are also listed. Care must be taken when comparing the calculated May 1975 fluxes with the July 1975 measured values. As shown in Table 5, the airborne concentrations of the trace metals were different during the two experiments. Note that the measured lead flux, 31.7 nanograms per square centimeter per day (ng/cm^2/day), is greater than the lead flux measurement given in Figure 4 of only 22 ng/cm^2/day. The difference exists because the above experiments measured daytime fluxes. The experiments corresponding to Figure 4 measured overall fluxes, during both day and night.

TABLE 4. CALCULATED AND MEASURED FLUXES TO FLAT SURFACES

	Measured Fluxes for the July 1975 Experiment (ng/cm^2/day)			Calculated Fluxes (ng/cm^2/day)	
	J_{top}	J_{bottom}	J_{sed}	J_{sed} July 1975	J_{sed} May 1975
Pb	31.7	7.0	24.7 ± 11%	29.2 ± 9%	28.9 ± 6%
Zn	12.0	3.82	8.18 ± 12%	6.5 ± 11%	7.7 ± 10%
Cd	0.238	0.085	0.153 ± 58%	0.224 ± 25%	0.448 ± 10%

TABLE 5. AIRBORNE CONCENTRATIONS DURING THE TWO ISOKINETIC IMPACTOR EXPERIMENTS

	July 1975 (ng/m^3)	May 1975 (ng/m^3)
Pb	1254 ± 3%	1160 ± 2%
Zn	127 ± 6%	131 ± 9%
Cd	4.1 ± 15%	11.6 ± 5%

Table 4 shows measured depositions on both upward-facing (top) and downward-facing (bottom) plates. Both sticky and unsticky surfaces were used; no significant differences in deposition were observed.

The bottom plate fluxes are considerably smaller than the top plate fluxes. This agrees with the results of Gregory (1961), who found a greater deposition of 32-μm diameter lycopodium spores on the top of a glass microslide than on the bottom, for small windspeeds.

In a separate experiment at the same site, the number of large particles with geometric diameters greater than 10 μm which had deposited on these flat plates was determined using an optical microscope. The ratio of large particles on the bottom plate to large particles on the top plate was 0.044. Thus it is likely that the trace metal deposition on the bottom plate was primarily due to small particles.

There are data in the literature which compare small particle deposition on upward- and downward-facing surfaces. Bullas (1953) has measured the deposition of fission-product activity from nuclear test explosions on the top and bottom of a flat surface. This activity is generally attached to condensation nuclei with diameters of less than 0.1 μm (Chamberlain, 1960). He measured a value of 0.7 for the ratio of bottom surface deposition to top surface deposition. Megaw and Chadwick (1957) produced a uranium fume and measured the deposition on top and bottom flat surfaces. The fume consisted of 83 percent by mass small particles with diameters of less than about 0.2 μm, but with some supermicron material. Their value of the ratio was 0.6.

These values are somewhat less than unity, which is consistent with the data and observations of Sehmel (1973). He found that gravity assists the turbulent transport of small particles on horizontal upward-facing surfaces by forcing the particles downward into regions of smaller eddies. This results in slightly greater fluxes on top surfaces than on bottom surfaces.

As an approximation, it is assumed in this analysis that the deposition of small trace-metal particles is equal on top and bottom surfaces. Thus the net sedimentation flux, ^{J}sed, is equal to the top plate flux minus the bottom plate flux. These values are also shown in Table 4.

It may be argued that brief gusts of wind in excess of the average 1.4 m/sec may be responsible for much of the deposition. This would especially apply to the large mass of submicron particles, since small particles have deposition velocities greater than sedimentation velocities in moderate winds. However, the maximum windspeed recorded during the experiment was only 4.4 m/sec. When the results of Sehmel (1973) for a 6.7 m/sec windspeed are used to predict deposition velocities of the submicron particles, it is found that the flux of these particles is indeed greater than the sedimentation flux. But either value is negligible compared to the supermicron flux.

It may also be argued that turbulent deposition of large particles causes increases over sedimentation deposition, even for smooth surfaces. Sehmel (1973) has shown that this effect is not noticeable for a 2.2 m/sec windspeed, although it becomes important at 6.7 m/sec. Because of the low windspeeds measured during the experiment, turbulent deposition is believed to have been unimportant.

EXPERIMENTAL ERRORS

All uncertainties in this study represent one standard deviation about the mean. Each measurement x_i is assigned an uncertainty σ_{x_i}, and the uncertainties are compounded according to:

$$\sigma_f^2 = \sum_i \frac{\partial f}{\partial x_i}^2 \sigma_{x_i}^2 \tag{13}$$

where f is any function calculated from the various x_i's, and σ_f is the standard deviation of f.

Measurements of the blanks are subtracted from all atomic absorption readings, and uncertainties of 100 percent are assigned to the blank values. In addition to the usual errors associated with atomic absorption, the error bars of Figure 5 also include the effects of nonideal impactor efficiency curves and errors in counting and measuring particles under the optical microscope. The uncertainties in the calculated fluxes are also determined from the above errors.

Other errors also affect the size-distribution measurements and the flux calculations. Some of these include wall losses and bounceoff in the impactor, nonisokinetic sampling, and using the Figure 5 stairstep distribution to approximate the actual distribution. These other errors are estimated below, but are not included in the error bars and uncertainties in tables and figures.

Wall losses in the Andersen impactor have been discussed by May (1964) and by Rao (1975). May found that the most significant wall losses occurred on the sieve above the top stage. When the impactor was calibrated in this study with atmospheric particles, the size-distribution of particles depositing at the center of the top stage sieve was measured. It was found that a significant mass deposited that was mostly soil-dust particles with geometric diameters greater than 40 µm. It is estimated that about 16 percent of the mass collected by stages A, B, and 1 deposited in this area. However, it is not likely that this extra mass included many trace-metal-containing particles because large soil-dust particles are poor scavengers.

May (1964) also predicted that losses result as large particles attempt to pass around one stage and proceed to lower stages. The size of this error has not been evaluated.

Rao (1975) found significant wall losses for large particles, especially near jet entraces on the top stages. He also found bounceoff to be a problem. As expected, the most significant bounceoff occurred when solid particles impacted on stainless steel plates. Sticky surfaces collecting liquid particles had negligible bounceoff. Similar results have been reported by Hidy (1974). To minimize bounceoff in the trace-metal experiments, sticky Teflon was used. However, the actual errors are unknown.

The errors due to nonisokinetic sampling can be estimated for windspeed and wind direction data obtained during the impactor runs. For the July 1975 experiment, the average windspeed was 1.4 m/sec while the inlet airspeed was 1.8 m/sec. According to Watson (1954), the ratios of measured-to-actual airborne concentrations for these conditions are 96 percent for 12-μm, 90 percent for 31-μm, and 84 percent for 37-μm equivalent diameter particles. Since the wind was gusty with speeds different from the average 1.4 m/sec, the true errors may be greater.

Errors due to the impactor not always facing into the wind can also be estimated. Frequent checks on the wind direction were made, and whenever the wind shifted by more than 20°, the impactor was realigned. A record of these realignments shows that the impactor could have been misaligned by about 30° for as much as one-fourth of the time during the run. For a windspeed equal to the inlet airspeed, Watson has predicted the ratios of measured to actual concentrations for a 30° misalignment. His values are 92 percent for 12-μm and 85 percent for 37-μm equivalent diameter particles. The sampling errors for the May 1975 run are slightly smaller than for the July experiment.

Calculations of the flux J have been based on the approximate stairstep distribution of Figure 5. By dividing each size range into several smaller stairsteps, so that the size-distribution is closer to a smooth curve, an estimate of the error is obtained. This was done using the raw data from the particle-size measurements which were accurate to ± 0.4 μm for a dp of less than 4 μm. The error was calculated to be less than 1 percent.

For the particles on the lower impactor stages which were too small to be counted, the maximum error in calculating the flux was estimated. It was assumed that all of the mass was at one of the dp endpoints of a stage rather than uniformly distributed across the dp range. The maximum error was calculated to be 3 percent of the total flux.

Another possible source of error is that the particles may change size as they deposit on the impactor plates. The assumption that the size-distributions of trace metals based on aerodynamic equivalent diameters are the same as the total distributions measured with the optical microscope may also be a source of error.

ANDERSEN IMPACTOR CUTOFF DIAMETERS

Generally it is assumed that the particle sizes on an impactor stage vary from one dp_{50} value to the dp_{50} value of the next stage. This is strictly true only for an ideal impactor where there is no overlap of particle sizes from one stage to the next. However, real impactors such as the Andersen sampler are highly nonideal. The calibration curves of Flesch et al. (1967) were used to estimate the cutoff diameters for each stage, and also the uncertainty in the cutoffs due to the nonideal nature of the curves.

The size-distributions of Figure 5 assume a uniform mass distribution with respect to log dp on each impactor stage. This yields only a stairstep approximation to the true distribution, but there is no physical basis for interpolating values between the cutoffs. To be consistent with the uniform mass assumption, it is assumed that a uniform mass distribution impinges upon an impactor stage with a known efficiency curve such as the one shown in Figure 6.

All particles greater than dp_{max} will be captured by the stage, while all particles smaller than dp_{min} will pass the stage. Particles between dp_{min} and dp_{max} will have various collection efficiencies depending on the shape of the curve.

The curves of Flesch et al. (1967) have been used to determine the dp_m cutoffs and σdp_m. Values are shown in Table 6. For the size-distributions of Figure 5, the dp_m and σdp_m values were recalculated for a flow rate of 13.2 liters per minute. The curves are from Flesch et al. (1967) for the calibration flow rate of 28.3 liters per minute. The values for stage 7 (not studied by Flesch et al.) were obtained by

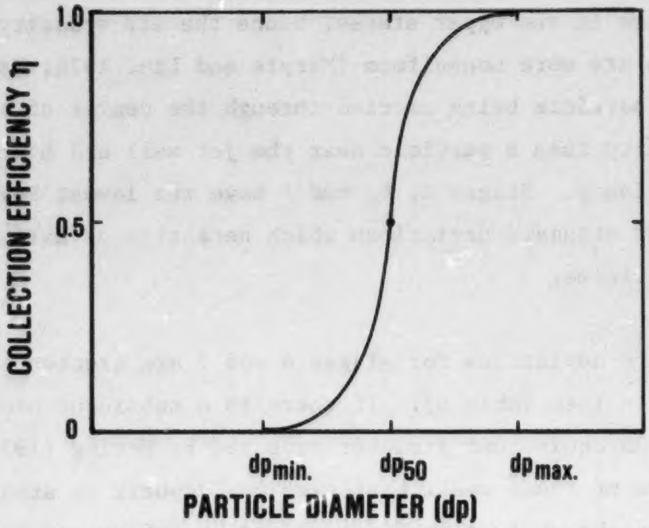

Figure 6. Impactor stage collection efficiency as a function of particle diameter dp, for a typical stage.

assuming the same shape efficiency curve as stage 6 but with a stage 7 dp_{50} value according to Andersen specifications.

TABLE 6. VALUES OF MASS MEAN CUTOFF DIAMETERS dp_m AND THE STANDARD DEVIATIONS FOR THE ANDERSEN IMPACTOR EFFICIENCY CURVES

Impactor Stage	dp_m (μm)	σdp_m (μm)
2	6.63	2.25
3	3.78	1.51
4	1.98	0.74
5	1.06	0.50
6	0.80	0.43
7	0.53	0.29

Inspecting the standard deviations, it is clear that the efficiency curves are highly nonideal. The large particle stages are in fact more nonideal than the lower stages. This is because the Reynolds numbers in the jets decrease in the upper stages, hence the air velocity profiles across the jets are more nonuniform (Marple and Liu, 1974; Marple et al., 1974). Thus a particle being carried through the center of a jet has a different velocity than a particle near the jet wall and hence a different impaction efficiency. Stages A, B, and 1 have the lowest Reynolds numbers and the greatest standard deviations which necessitates calibration with atmospheric particles.

The standard deviations for stages 6 and 7 are greater than 50 percent of the dp_m values (see Table 6). If there is a submicron peak between 0.1-μm and 0.5-μm equivalent diameter measured by Hering (1975), then a sizable fraction of these small particles may deposit on stages 6 and 7. Thus the large peaks at 1 μm in Figure 5 may be influenced by submicron material.

DISCUSSION OF TRACE-METALS DEPOSITION STUDIES

The airborne size-distributions of lead, zinc, and cadmium at Caltech in Pasadena, California, are bimodal. The upper mode which is located above 10 μm in equivalent diameter, is considerably stronger for zinc and cadmium than for lead.

Comparing the calculated and measured sedimentation fluxes shows that reasonable agreement has been obtained. Because the sedimentation flux is about 70 percent of the total top plate flux, it is concluded that sedimentation is the dominating deposition mechanism for these trace metals at this site

The size-distribution can be used to predict the mass deposition of these trace metals on a flat surface under ambient conditons. Using sedimentation as the mechanism for deposition, it is calculated that over 95 percent of the deposition mass is due to the fraction of particules greater than 10 µm in aerodynamic diameter. The deposition mass from sedimentation is about 70 percent of the deposition mass from all mechanisms on an upward-facing flat plate for each of the trace metals.

The percentage of particles greater than 10 µm in aerodynamic diameter is 17, 32, and 37 percent for lead, zinc, and cadmium, respectively. On the basis of the deposition data and the size-distribution measurements, it is concluded that small particles play only a minor role in the deposition process. Rather, sedimentation of a few large particles dominates the mass deposition at this site for these trace metals.

The deposition velocity of a species may decrease as the species moves away from its source, if the depositional loss of particles from the atmosphere is faster than particle growth. The deposition velocity of lead, for example, decreases from 1.8 cm/sec near a freeway to 0.07 cm/sec in a remote area.

Although sedimentation of large particles may dominate mass deposition near the source, this may not be the case far from sources. Once the large particles have deposited out, the smaller material may remain airborne for considerable periods of time. These particles may eventually deposit by diffusional deposition.

In some cases, attachment of small particles to larger particles may be important. For example, the lead size-distribution near long stretches of rural highways may be dominated by the very small particles produced by steadily cruising automobiles. Far from the roadway, attachment to large dust particles may increase the lead MMED.

The above analysis applies only for deposition on smooth surfaces. Deposition velocities on rough natural surfaces are likely to be greater than sedimentation velocities, even for large particles.

SECTION IV

EXAMPLES OF MASS BALANCES

AUTOMOTIVE LEAD IN THE LOS ANGELES BASIN

A material balance carried out on automobile-emitted lead in the Los Angeles Basin, was based on estimates made of the daily consumption of lead by automobiles and the amounts exhausted to the atmosphere, deposited on the land and roadways, and advected out of the Basin. The mass flows are based on new measurements of atmospheric lead concentrations, particle size-distributions, the surface deposition of lead, lead in surface water runoff, and data from the literature. The area for which the calculation is made includes the major population centers of Los Angeles and Orange Counties.

For a conservative species, such as lead, the terms appearing in the material balance are well defined with respect to a given geographical area. As examples, the total lead emitted to the atmosphere, lead deposition on surfaces, and the quantity advected by the winds past the borders of the region are all exact quantities for any given time period. Such quantities can be estimated as shown below, but their values are only approximate at this time. The estimates will, however, be useful in a number of possible applications. The relative contributions of Los Angeles and nearby sources to atmospheric lead concentrations in regions downwind of the Basin can be estimated. Similar calculations can be made on the lead input to coastal waters from various sources. Such results should be of value to making policy decisions related to nondegradation of air quality and to water quality standards. It will also be possible to estimate the flow of certain other trace pollutants from the lead balance.

Consumption of Lead

Although detailed information on the consumption of alkyl lead additives is not available, the lead consumption rate for Los Angeles can be estimated using known data. In 1972, the average distribution rate of taxable gasoline for the State of California was 104 million liters per day (California State Board of Equilization, 1972). During the same year Los Angeles and Orange Counties accounted for 41.4 percent of the automobiles, motorcycles, and trucks in California (Carey, 1973). If it is assumed that gasoline consumption is proportional to the number of motor vehicles, the consumption rate for the Los Angeles region is 42.9 million liters per day. The average concentration of lead in Southern California gasoline for the winter 1971-72 was 0.56 ± 0.06 grams per liter (g/l). This gives an average 1972 lead consumption rate of 23.7 ± 2.4 metric tons per day (tons/day). (For bookkeeping purposes, one more significant figure than justified is carried).

Estimates of the average concentration of lead in Southern California gasoline were derived from 1971-1972 U.S. Bureau of Mines data (Shelton, 1972). The average premium gasoline contained 0.73 g/l of lead, the average intermediate grade gasoline 0.56 g/l, and the average regular grade 0.40 g/l. A composite value for so-called "third-grade" gasolines was subdivided for this analysis into "low lead" gasoline with 0.12 g/l and "unleaded" with 0.01 g/l. The usage of this subdivision may not necessarily correspond to what one buys at a gasoline station. For example, many actual "low lead" gasolines are probably classified by the Bureau of Mines as "regular."

According to the Los Angeles Air Pollution Control District, 62.9 percent of the gasoline sold in Los Angeles County in the summer of 1972 was premium. An increasing fraction of low compression vehicles on the road and the relative increase in the consumption of lower lead gasoline limits the validity of this percentage to 1972. The remainder is divided among intermediate, regular, "low lead," and "unleaded" grades. Because the intermediate grade lead concentration falls within the range of concentrations found in regular gasoline, and because of the low volume sale of "unleaded" gasoline in 1972, little uncertainty is introduced by not including these grades in this study. Thus, the two cases considered represent upper and lower limits for lead consumption; 62.9 percent premium and 37.1 percent regular, and 62.9 percent premium and 37.1 percent "low lead." The average lead content from these two cases is 0.56 ± 0.06 g/l where the uncertainty refers to the two possible extremes.

The Los Angeles County Air Pollution Control District (Lemke, 1971) estimates that during 1972 350 tons/day or about 5 x 10^5 liters/day of gasoline was lost by evaporation from automobile fuel systems and during gasoline handling operations. If the tetraethyl lead fraction does not change during evaporation, then approximately 0.3 tons/day of lead in tetraethyl lead vapor was emitted into the atmosphere, and the remainder, 23.4 tons/day was consumed by automobiles.

Nature Of Lead Emissions

Hirschler et al. (1957, 1964) showed that the size and amount of lead-containing particles were sensitive functions of driving mode. At cruising speeds the exhaust fraction varied between 14 and 54 percent. During full throttle acceleration, however, large amounts of lead were reentrained from the exhaust system giving exhaust fractions up to 200 percent of the input. Subsequent studies by Mueller et al. (1964), Ter Haar et al. (1972), and Habibi (1970, 1973) confirmed Hirschler's general results. Ter Haar et al. (1972) found that the exhaust fraction was small for automobiles with new exhaust systems but increased with age; this indicated that a break-in period of several thousand miles was necessary before the exhaust system deposits stabilized. Thus an accurate picture of typical lead emissions under consumer conditions can only be obtained by monitoring lead emissions for many thousands of miles.

Hirschler et al. (1957, 1964) studied three automobiles over periods which included both uncontrolled suburban driving and programmed chassis dynamometer tests. They found that three cars with 27,000, 19,300, and 9,800 accumulated miles (43,000, 31,000, and 16,000 km) retained 21.2 percent, 27.5 percent, and 23.1 percent, respectively, of the input lead. Ter Haar et al. (1972) conducted a similar study on one car, but also attempted to construct a complete mass balance for the lead by collecting the exhausted lead in a cyclone separator and total filter. After 12,000 miles (19,300 km) over a fixed route, 30 percent of the input lead remained in the oil, oil filter, and exhaust system, and 54 percent had been exhausted. Ter Haar et al. (1972) speculated that the remaining 16 percent was lost during handling of the filter and exhaust system.

For an automobile operated under simulated consumer test conditions, Habibi (1973) found an emission rate of 89 percent between 20,000 and 33,000 accumulated miles (32,000 and 53,000 km). However, Habibi's results for these mileages are probably not representative of the total vehicle population since they do not take into account the break-in periods for new cars and cars with new mufflers.

To estimate the amount of lead exhausted, the retention factors (i.e., percent of lead remaining in the car) of Hirschler et al. (1957, 1964) and Ter Haar et al. (1972) are assumed representative of the total vehicle population. A retention factor of 30 percent is used for the Ter Haar results without trying to account for the missing 16 percent. This is a consistent application of the Hirschler and Ter Haar data since Hirschler et al. measured only the lead remaining in the car and did not construct a total mass balance. The average retention factor for the four automobiles sampled was 25 ± 4 percent. Thus, of the 23.4 ± 2.4 tons/day of lead burned, 5.8 ± 1.1 tons/day is retained in the cars, and 17.6 ± 2.6 tons/day (by difference) is exhausted to the atmosphere. (Because of the changing nature of gasoline consumption, this exhaust rate applies strictly only to 1972.) The use of the Hirschler and Ter Haar retention factors implies muffler and exhaust system changes at about 27,000-mile

(43,500-km) intervals although the actual interval may be longer. Such a change will restore the automobile to a low emission state and will entail another break-in period. Firm data are not available to evaluate these effects, however.

Brief (1962) has shown that auto exhaust lead contains both a particulate fraction and an organic, vapor-phase function. Measurements on eight pre-1961 European and English cars showed that the vapor-phase component was about 12 percent of the particulate component. Because of his sampling scheme, however, the particulate lead measured by Brief probably consisted primarily of particles smaller than about 9 μm which according to Habibi (1973) (see below), make up 43 percent by weight of the particulate exhaust. Thus, if Brief's results can be applied to Los Angeles automobiles, approximately 0.9 tons/day of organic, vapor-phase lead and 16.7 tons/day of particulate lead are exhausted. Recent measurements of particulate and vapor-phase organic lead near roadways by Skogerboe (1974)* also indicate a significant organic lead contribution. The fate of the vapor-phase lead is discussed later. Lead emissions from nonautomotive industrial sources are small (∿0.3 tons/day) and are not included in the mass balance.

Of the lead which remains in the car, one-third of one-half is in the oil and oil filter (Hirschler et al., 1957, 1964; Ter Haar et al., 1972.) The fate of used motor oil is not well documented. There is some disposed directly into the sanitary sewer system, uncontrolled disposal onto the ground, and limited reclamation for reuse (Bowen, 1972.)

Lead Measurements

The material balance method developed in this Section is based on measurements of atmospheric particle size-distributions, surface deposition fluxes and atmospheric lead and carbon monoxide concentrations. Measurements were made to provide data which were relative to the reference year 1972, and based on a consistent set of experimental and analytical techniques. Earlier measurements of particle size-distributions (Robinson and Ludwig, 1967), airborne lead concentrations (Tepper, 1971; National Air Surveillance Networks, 1973; Public Health Service, 1965; Colucci et al., 1969), lead deposition on *Avena sativa* (wild oats), (Rabinowitz, 1972), and carbon monoxide concentrations (Public Health Service, 1965; Lemke, 1971; Colucci et al., 1969) have been reported for the Los Angeles area.

---

* Skogerboe, R. K., private communication (1974).

Lead deposition was measured at Pasadena for ten different 1- or 2-week sampling periods between November 1972 and February 1974. A 1- week synoptic measurement of deposition was made at Pasadena and five other locations in the Los Angeles Basin during August 1973. Deposition measurements were also made at three locations near a freeway in May 1973 at two coastal islands, and at four sites each along the coast, in the Mojave Desert, in the San Gabriel-San Bernardino Mountains, and in the Coachella Valley during the summer of 1973. During each of these measurement periods, lead deposition in Pasadena was also measured. Size-distribution measurements were made at Pasadena and a freeway. Size-distribution and atmospheric lead concentrations were also measured at five sites in the Los Angeles Basin during the 1972 and 1973 phases of the California Aerosol Characterization Experiment (ACHEX) (Hidy, 1973.)

Experimental errors are expressed as one standard deviation about the mean and are related only to variations about the mean unless noted otherwise. These errors are not related to individual uncertainties in each separate measurement. Uncertainties for derived quantities are compounded in the usual manner.

Removal Of Lead From The Atmosphere: Deposition

Of the 16.7 tons per day of particulate lead which is exhausted, most is in the form of lead halide particles; however, other chemical species have been identified. Depending on the particle size, a number of environmental pathways are available. For example, very large particles (dp > 10 μm) settle rapidly. (Unless otherwise specified, all particle diameters are for the aerodynamically equivalent, unit-density spheres.) Smaller particles may remain airborne for a longer period, but some eventually deposit in the urban area by convective diffusion to surfaces. The mechanisms for particle removal have been discussed by Chamberlain (1967a, 1967b) and Sehmel (1972) for relatively well-defined smooth and rough surfaces. A knowledge of the particle size-distribution is important in evaluating these effects.

The size distribution of auto exhaust lead aerosol has been studied by many investigators (Hirschler et al., 1957; Hirschler and Gilbert, 1964; Mueller et al., 1964; Ter Haar et al., 1972; Habibi 1970, 1973; Moran and Manary, 1970; Lee et al., 1971; Ninomiya et al., 1971; Ganley and Springer, 1974). Only Habibi (1973) and Ter Haar et al. (1972) attempted to simulate actual driving conditions, and of these, the study by Habibi was most detailed. Consequently, much of the following discussion is based on Habibi's results.

Habibi (1970) sampled auto exhaust aerosol at the end of a 12-meter long wind tunnel with an isokinetically operated cascade impactor. Coarse particles deposited in the wind tunnel were also measured and assigned to the first impactor stage. For an automobile operating solely on a chassis dynamometer programmed to the 1968 Federal Mileage Accumulation Schedule, the mass median diameter of the particulate lead increased from about 1 μm at 5,000 accumulated miles (8,000 km) to greater than 15 μm at 28,000 miles (45,000 km). At this latter mileage, 57 percent of the mass of lead was associated with particles larger than 9 μm in diameter. A car which had been driven on the road under typical consumer conditions for 15,000 miles (24,000 km) followed by about 18,000 miles (29,000 km) on the programmed chassis dynamometer also gave a lead aerosol with 57 percent by weight in particles larger than 9 μm in diameter and a mass median diameter greater than 15 μm.

Ter Haar et al. (1972) tested 26 cars with 17,000 to 92,000 miles (27,000 to 148,000 km) of service and concluded that 55 percent of the emitted lead was in "coarse" particles (i.e., particle diameters greater than about 5 μm). For an automobile operated for 12,000 (19,300 km) miles on a mileage accumulation route, Ter Haar et al. also found that 58 percent of the emitted lead was as course particles. (As noted above, however, 16 percent of the input lead could not be accounted for.) Ninomiya et al. (1971) measured the size-distribution of auto exhaust aerosol and found that approximately 20 to 30 percent by weight of the lead was a "coarse material" (500 μm < dp < 5,000 μm) for a dynamometer cycle consisting of a cold start followed by four Federal test procedure driving cycles.

For the mass balance analysis presented here, it is assumed that the particle size-distribution of auto exhaust lead at 33,000 accumulated miles (53,000 km) measured by Habibi (1973) is typical of Los Angeles cars. From the known age distribution of California automobiles and the mileage accumulation rate of Los Angeles automobiles (Lees et al., 1972), an average accumulated mileage of 57,000 (92,000 km) is estimated. This distribution is plotted in Figure 7 along with lead size-distribution taken at a receptor site in Pasadena which was not in the immediate influence of traffic. Dp is the aerodynamic, unit-density particle diameter. In the receptor site distributions, only 2 to 7 percent of the mass is in the greater than 9-μm fraction as compared to 57 percent for the auto exhaust distribution. This is consistent with the size-distributions determined at receptor sites in the ACHEX study (Hidy, 1974) which also show very little mass (<5 percent) above 9 μm. In Figure 8, differential mass distributions for lead aerosol at a site 1 meter from a freeway and at the Pasadena receptor site show that the large particle mode $\bar{D}p > 7$ μm) at the freeway is severely attenuated at the receptor site. Size-distribution measurements by Daines et al. (1970) also show a decrease in large particle lead with increasing distance from a highway. The dashed lines in Figure 8 are based on the assumption that the smallest particle size is 0.01 μm and the largest is 50 μm.

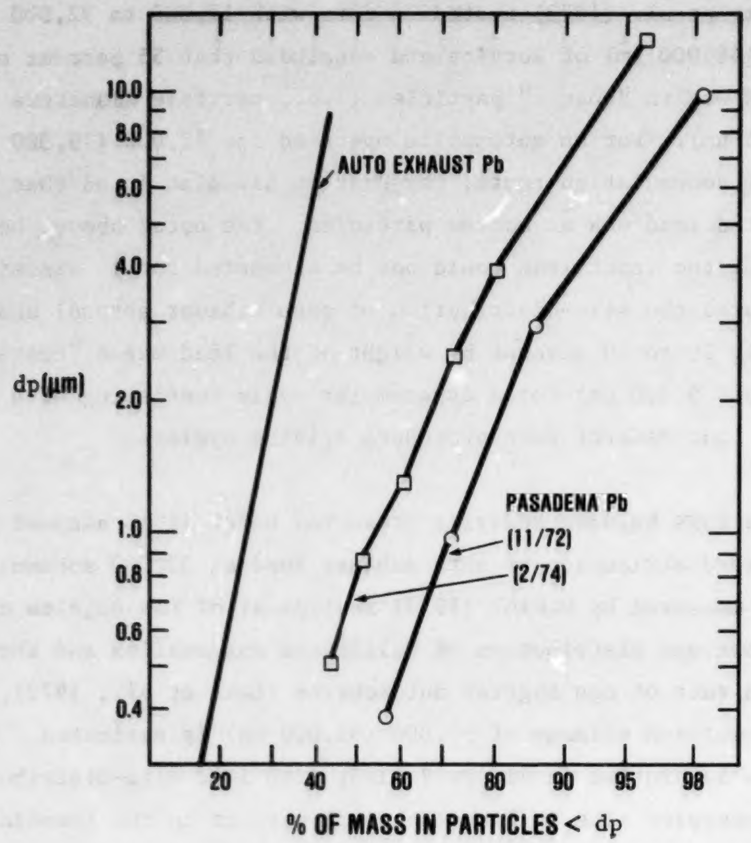

Figure 7. Cumulative mass distributions for lead aerosol in auto exhaust and in ambient air at Pasadena. (Dp is the aerodynamic, unit-density particle diameter.)

The difference between the source and receptor size-distributions is due in part to the rapid deposition of very large particles near the roadway. Habibi (1970, 1973) found that approximately one-half to two-thirds of the greater than 9-µm fraction deposited within 7 meters of the automobile exhaust pipe in the wind tunnel experiments. In this current analysis, it is assumed that all of the greater than 9-µm fraction deposits on or near the roadway in what is termed "near" (source) deposition. Although a cutoff at 9 µm is somewhat arbitrary, Heichel and Hankin (1972) found that lead-containing particles deposited on trees adjacent to a heavily traveled road ranged in aerodynamic diameter from 7 to 32 µm with a mean of 17 µm. The near deposition fraction is 57 percent of the exhausted lead for which an uncertainty of ± 10 percent is assigned to

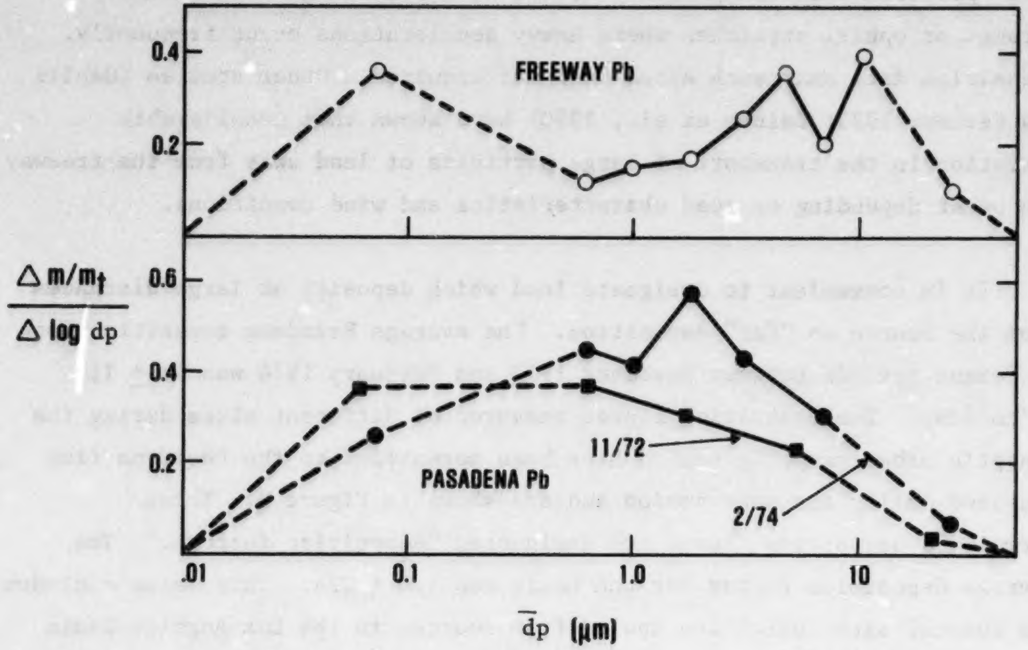

Figure 8. Differential mass distributions for lead at 1-meter from a freeway and for Pasadena.

account for variations among automobiles and muffler changes at various mileages. This amounts to 9.5 ± 2.2 tons/day.

Deposition measurements at 1, 30, and 150 meters from a freeway, at which the traffic flow was unidirectional and slightly downhill, gave a factor of 15 decrease between the sites at 1 and 30 meters. The integrated deposition over this 150-meter strip could account for only about 10 percent of the near deposition expected from average emissions based on the above considerations. However, Habibi (1973)* has pointed out that most of the large particle emission probably occurs at locations such as freeway onramps or uphill stretches where heavy accelerations occur frequently. Deposition data near such sites were not acquired. Other studies (Cahill and Feeney, 1973; Daines et al., 1970) have shown that considerable variation in the transport of large particles of lead away from the freeway can occur depending on road characteristics and wind conditions.

---

* Habibi, K., private communication (1973).

It is convenient to designate lead which deposits at large distances from the source as "far" deposition. The average Pasadena deposition for different periods between November 1972 and February 1974 was 45 ± 11 $ng/cm^2/day$. The deposition fluxes measured at different sites during the synoptic urban sampling period have been normalized to the Pasadena flux measured during the same period and are shown in Figure 9. These normalized deposition fluxes are designated "deposition factors." The average deposition factor for the basin was 1.0 ± 0.4. This value excludes the coastal sites which are upwind from sources in the Los Angeles Basin most of the time. In Figure 9 the squares correspond to current surface deposition measurements, the open circles to the wild oats (*Avena sativa*) data (Rabinowitz, 1972), and the triangles to the airborne data (Tepper, 1971); National Air Surveillance Networks, 1973; Hidy, 1973). The solid circles indicate specific locations, e.g., Pasadena. The southern boundary of the basin is taken to be the Pacific Coast and the northern boundary the first crest of the San Gabriel Mountains (e.g., Mt. Wilson.)

Related data such as the atmospheric concentrations of lead and the concentrations of lead on the tops of wild oats (*Avena sativa*) can be used to check whether current deposition measurements are characteristic of the Los Angeles Basin. Studies by Motto et al. (1970), Dedolph et al. (1970), and Rabinowitz (1972) have shown that lead in the tops of grass comes primarily from lead aerosol while the soil contributes only 2 to 3 parts per million (ppm) (dry weight) of lead. Deposition on horizontal surfaces and on oats depends primarily on the atmospheric concentrations of lead and is relatively insensitive to the particle size-distributions and wind conditions (Chamberlain, 1967a, 1967b; Sehmel, 1972.) Thus deposition

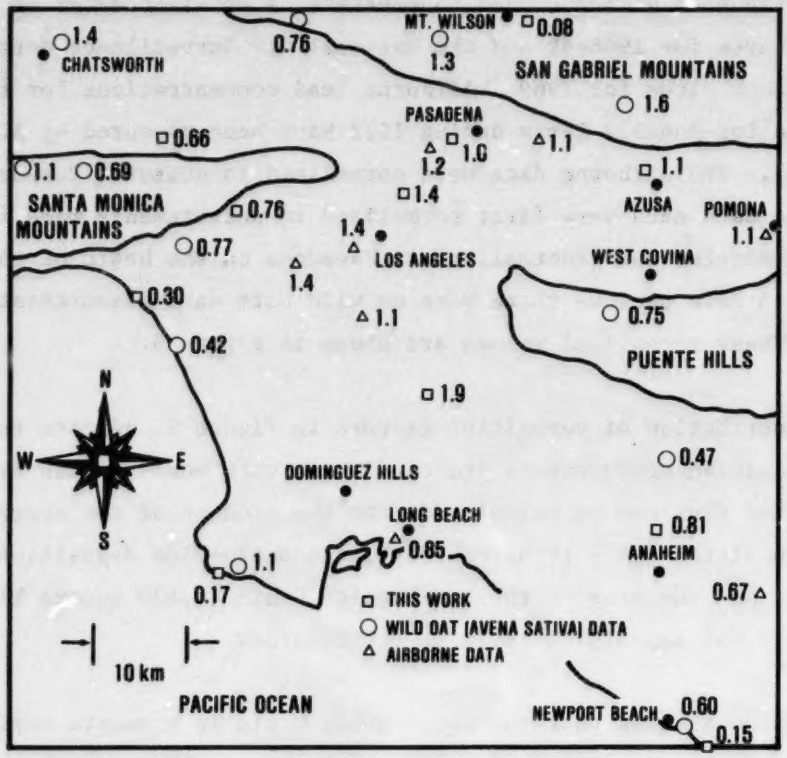
1.4
CHATSWORTH
0.76
MT. WILSON
0.08
1.3
SAN GABRIEL MOUNTAINS
1.6
PASADENA
0.66
1.2
1.0
1.1
1.1
1.1
0.69
SANTA MONICA MOUNTAINS
1.4
AZUSA
POMONA
0.76
1.4
1.1
0.77
LOS ANGELES
WEST COVINA
1.4
0.30
1.1
0.75
0.42
PUENTE HILLS
N
W
E
S
1.9
0.47
DOMINGUEZ HILLS
LONG BEACH
0.81
0.85
1.1
ANAHEIM
0.17
0.67
THIS WORK
WILD OAT (AVENA SATIVA) DATA
AIRBORNE DATA
10 km
PACIFIC OCEAN
NEWPORT BEACH
0.60
0.15

Figure 9. Distribution of deposition factors in the Los Angeles Basin.

factors based on normalized concentrations of atmospheric lead and lead on the tops of wild oats should be equivalent to flat surface deposition measurements used here.

The Rabinowitz (1972) measurements of lead concentrations in wild oats between December 1971 and January 1972 at many sites in the Los Angeles area represent the accumulation of lead over the whole growing season. Lead is not washed off *Avena* by rainfall (Rains and Thornton, 1970). Tepper

(1971) has reported airborne lead concentrations at eight sites in the Los Angeles area for 1968-69 and the National Air Surveillance Networks (1973) for four sites for 1969. Airborne lead concentrations for two sites in the Los Angeles Basin during 1972 have been measured by ACHEX (Hidy, 1973). The airborne data were normalized to measured Pasadena values. The oats data were first normalized to measurements made in central Los Angeles and renormalized to Pasadena on the basis of the airborne lead data because there were no wild oats data measurements in Pasadena. These normalized values are shown in Figure 9.

The distribution of deposition factors in Figure 9 indicate that current deposition measurements are consistent with measurements by others. The deposition flux can be calculated from the product of the average Pasadena deposition (45 ± 11 $ng/cm^2/day$), the Basin-wide deposition factor (1.0 ± 0.4), and the area of the Los Angeles Basin (4,430 square kilometers). The resultant far deposition is 2.0 ± 1.0 tons/day.

This value assumes that the Los Angeles Basin is a smooth surface. Vegetation and manmade structures will alter this number, but the magnitude of these effects is difficult to evaluate. The deposition on grassy surfaces can be estimated from the deposition velocities of Sehmel et al. (1973) for 0.7-cm grass and an 8-kilometer per hour (km/hr) wind. If the average atmospheric concentration is taken to be 2.4 $\mu m/m^3$ (the average for all measurements in this study) and the Pasadena size-distribution assumed to be typical of the Basin, then the estimated lead deposition for grass is about 40 ng/cm^2 (of land area) per day, which is not significantly different from the experimental value for the Teflon surface. Deposition on vertical surfaces will also contribute to the total far deposition. The vertical surface of buildings is about 25 percent of the total land area, and only about one-fourth of this is exposed to the wind at any given time. Thus, the additional deposition on buildings is probably small. Trees will also increase the far deposition term, but this effect is difficult to estimate. In general, more research is necessary to clarify these uncertainties.

Airborne Lead: Removal By Wind

Airborne lead an carbon monoxide, both of which result almost completely from automobile exhaust in the Los Angeles area, are known to be positively correlated (Public Health Service, 1965; Colucci et al., 1969). On the time scale of the air flow through the Los Angeles Basin, carbon monoxide is unreactive and therefore conserved. Only on very smoggy days with high oxidant concentrations will carbon monoxide be removed at rates on the order of 1 percent per hour by reaction with a hydroxide (Weinstock and Niki, 1972; Wilson, 1972). To estimate the amount of lead which is blown out of the Basin, the Basin is considered to be a continuously stirred flow reactor. In this approximation the input and output flows of carbon monoxide are equal, and the lead output flow can be estimated from the relationship.

$$q_{pb} = q_{CO} \overline{[Pb]/[CO]} \qquad (14)$$

where q_i is the mass flow rate of species i out of the Basin and $\overline{[Pb]/[CO]}$ is the average value of the ratio of lead to carbon monoxide at receptor sites in the Basin. This approximation implies a constant proportionality between lead and carbon monoxide throughout the atmospheric mixing layer. Although vertical profiles of lead concentrations are not available, this assumption is reasonable because the dominant mechanism for the mixing of both species is eddy diffusion which will disperse both the gas and the aerosol (of which about 70 percent by weight is in the submicron fraction) in a similar manner.

Lead and carbon monoxide concentrations at five different sites in the Los Angeles Basin are available for 1972, 1973, and 1974 from current studies and from the ACHEX measurements. With the exception of one sampling period, all the lead measurements were made by high-volume sampling with Whatman 41 filters. Simultaneously, lead concentrations were sampled at 2-hour intervals by low-volume sampling with Gelman GA-1 membrane filters. For the 1973 ACHEX measurements, the ratio of "high-volume" lead to "low-volume" lead was 0.86 ± 0.08 where "low-volume" lead is the lead concentration determined by summing and averaging the low-volume filters over the high-volume sampling period. The high-volume filter data is used because of the greater possibility of systematic error (e.g., from contamination) involved in the handling of the low-volume filters. However, within the accuracy of the treatment in this analysis, no significant difference results from the choice of one or the other set of data.

The average lead-to-carbon monoxide (Pb/CO) ratios for the sites are given in Table 7 and the average for all sites is 0.69 ± 0.18 $\mu g/m^3$ lead/ppm carbon monoxide. The Pomona site is at the eastern border of the study region and the Rubidoux site is further east and outside the study region. Consequently Pb/CO ratios at these sites should be representative of air leaving Los Angeles since the major air flow is toward the east and north. The close agreement between Pb/CO at these sites and $\overline{\text{Pb/CO}}$ implies that the continuously stirred flow reactor formalism is a reasonable approximation.

TABLE 7. Pb/CO AT VARIOUS SITES IN THE LOS ANGELES BASIN

Site and Number of Sampling Days	Pb/CO ($\mu g/m^3$/ppm)
Pasadena (10)	0.46
Pomona (7)	0.74
West Covina (5)	0.79
Dominguez Hills (2)	0.81
Rubidoux (3)	0.65
Average	0.69 ± 0.18

When the $\overline{\text{Pb/CO}}$ ratio is adjusted for nonautomotive carbon monoxide and converted to a dimensionless weight ratio, the ratio is $6.2 \pm 1.6 \times 10^{-4}$. On the basis of seven mode cycle data, the Los Angeles Air Pollution Control District estimates that 7,200 tons of carbon monoxide was emitted each day by automobiles during 1972. Orange County adds an additional 20 percent (State of California, 1972), bringing the total to 8,600 tons/day.

An uncertainty of ±50 percent is assigned to this emission although the uncertainty may be even larger. The resulting rate of removal of particulate lead by advection is then 5.3 ± 3.0 tons/day.

In addition to the particulate airborne lead there is also a vapor-phase, organic component. Purdue et al. (1973) found the organic component to be about 10 percent of the total for six American cities. Skogerboe (1974)* measured organic fractions ranging between 4 and 12 percent at a receptor site in Fort Collins, Colorado. The work for this current report was conducted over a 3-day period in June 1974 and measurements of the organic component were found to be 6 ± 1 percent of the total Pasadena airborne lead. If this is typical of the Los Angeles region, 0.3 ton/day of vapor-phase lead is removed by advection. The difference between the input of organic lead (1.2 tons/day) and the output is due to photolysis of the organic lead vapor to produce a lead-containing aerosol (Milde and Beatty, 1959). Eventually all of the vapor-phase lead will decompose to an aerosol.

Lead Input To The Coastal Waters

The input routes to the coastal waters may include atmospheric deposition, rainout-washout, rainy weather runoff, dry weather runoff, discharge of treated sewage, and direct discharge of untreated wastes. These are all considered here with the exception of direct discharge of untreated wastes.

Because of the lack of data on the particle collection properties of the ocean surface, the estimate of the atmospheric deposition on the coastal waters is based on dry deposition measurements on the coastal islands. As noted earlier, the lead deposition rates on the standard Teflon collector and on a crystallization dish filled with water were the same. It is recognized that the dynamics of the ocean surface are quite different from those of the crystallization dish, and wave action may alter the particle deposition velocity at the ocean surface.

---

* Skogerboe, R. K., private communication (1974).

The deposition fluxes of lead on Santa Catalina Island and San Clemente Island during the summer of 1973 are plotted as a function of distance from the coastal baseline in Figure 10. The open squares in Figure 10 are deposition measurements from this work, the solid square is the deposition measurement by Patterson and Settle (1974), and the circles are the equivalent flat-surface deposition fluxes from the *Avena sativa* data (Rabinowitz, 1972). Rabinowitz (1972) has measured the concentration of lead in the tops of wild oats on San Nicolas, San Clemente, Santa Barbara, and Santa Catalina Islands, and along the coast. From deposition factors calculated from these data, equivalent flat surface deposition fluxes have been derived and are also plotted in Figure 10. A soil contribution of 2 ppm (dry weight) for the oats data was subtracted. The coastal deposition value in Figure 10 is the average of the surface deposition and oats data.

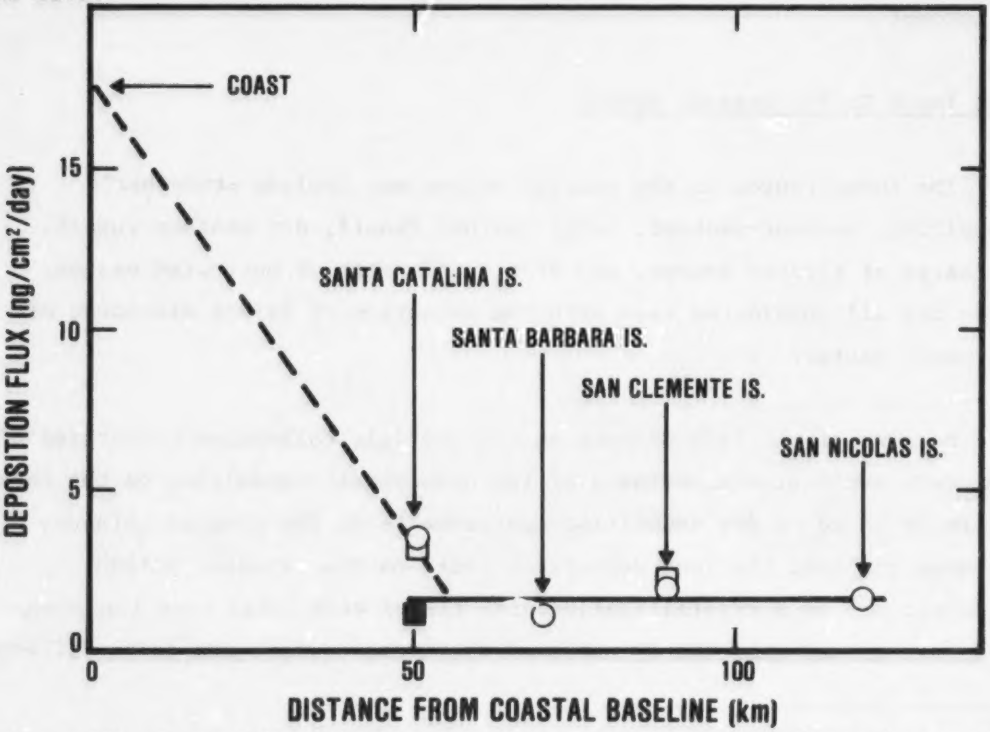

Figure 10. Deposition of lead as a function of distance from the coast.

Patterson and Settle (1974) have measured the surface deposition of lead on Santa Catalina Island for the 2-week period immediately following measurements in this current study and found a flux of 1.4 ng/cm^2/day as compared with a value of 3.3 ng/cm^2/day reported here. They also measured the lead-206 to lead-207 (^{206}Pb/^{207}Pb) ratios for the Catalina lead and the lead depositing in Pasadena and found a significant difference (1.171 and 1.193 ng/cm^2/day, respectively). Since sources of lead are different if the Catalina ^{206}Pb/^{207}Pb ratios differed by 0.3 percent from the Los Angeles lead ratios, they concluded that the lead depositing on Catalina during their measurement did not originate in Los Angeles air. This is consistent with the local meteorology. The prevailing wind pattern during the year is onshore flow during the day. At night, weak offshore drainage winds converge with the normal onshore flow. The western edge of the convergence zone is poorly defined, but may extend as far offshore as the eastern edge of Santa Catalina Island (DeMarrais et al., 1965.) Thus Santa Catalina can occasionally receive Los Angeles air, but except under Santa Ana conditions (east winds from the mountains and deserts), the islands which are farther offshore do not receive Los Angeles air.

Hidy et al. (1974) measured an average atmospheric lead concentration of 120 nanograms per cubic meter (ng/m^3) on San Nicolas Island (about 120 km from the coast) during the summer and fall of 1970. This corresponds to a surface deposition rate of about 2 ng/cm^2/day which is in reasonable agreement with the Patterson and Settle value of 1.4 ng/cm^2/day for Santa Catalina and the value reported here of 2.4 ng/cm^2/day for San Clemente Island. The somewhat higher value of Santa Catalina deposition in this current study (3.3 ng/cm^2/day) may represent a slight penetration of Los Angeles air, although no isotopic ratio measurements were made to confirm this. Early morning east winds on Santa Catalina were recorded on 5 days during these measurements, but not at all during the Patterson-Settle measurement. The deposition of cadmium on Santa Catalina was also somewhat higher than on San Clemente Island (Davidson et al., 1974).

The interpretation of the coastal island data assumes, then, that the influence of Los Angeles beyond Santa Catalina Island is negligible. Because deposition data between the coast and Catalina are not available, a simple linear interpolation (the dashed line in Figure 10) is used to estimate the decrease in deposition over this region. The "background" or non-Los Angeles lead is represented by the solid line in Figure 10 and is the average of Patterson and Settle's Catalina flux and the fluxes for the outer islands. The dashed line in Figure 10 defines a region of influence of Los Angeles extending to about 55 km from the shore, which for a linear coastal distance of 80 km corresponds to an area of 4,400 km^2. The average (dry) deposition flux over this region is 0.35 tons/day or 120 tons/year assuming 346 "dry" (i.e., rainfall less than 2.5 mm/day) days (U. S. Department of Commerce, 1968-73). Further measurements are necessary to define the origin of the "background" lead.

Chow et al. (1973) and Bruland et al. (1974) have measured lead accumulation rates in the ocean sediment of 4.7 $ng/cm^2/day$ in the San Pedro Basin (∿ 30 km for the coast), 2.5 $ng/cm^2/day$ in Santa Monica Basin (∿ 50 km from the coast), and 5.7 $ng/cm^2/day$ in the Santa Barbara Basin (∿ 30 km from the coast). The Santa Monica and San Pedro Basins are directly off Los Angeles while the Santa Barbara Basin is off Santa Barbara, about 100 km northwest of Los Angeles. Although these accumulation rates are of the same order as the deposition fluxes shown in Figure 10, their interpretation is complicated by various factors: the influence of sewage outfalls, a combination of advective ocean transport and settling, and dissolution during settling. Thus a direct comparison between these accumulation rates and deposition measurements is not possible, but the general agreement tends to support our interpretation of the deposition data.

The lead input to the coastal waters associated with rainout-washout can be calculated from the average annual rainfall over the coastal waters and the lead content of the rainfall. The average rainfall at three coastal sites and Santa Catalina Island is 30 cm per year (U.S. Department of Commerce, 1968-1973). In 1966-67 Lazrus et al. (1970) measured the flux of rainfall lead on Santa Catalina to be 25 $ng/cm^2/cm$ of rain. Thus the lead input to the region of influence defined by the deposition measurements is 30 tons per year.

Although positive identification of the origin of the rainfall lead has not been made, meterological data strongly suggest Los Angeles as the source. During the period of heaviest rain, November through February, the majority of the winds are from the quadrant centered on east-east northeast with an average speed of about 18 km/hr (DeMarrais et al., 1965). Such winds carry Los Angeles air well out over the ocean. In fact, the region of influence of the winds from Los Angeles may be larger than the region of influence determined from the deposition measurements. However, no data are available to confirm this.

In addition to the direct input by rainout-washout, rain storms will wash lead-containing particles into the storm sewers and ultimately into the coastal waters. Lead in runoff results primarily from street dirt. Soluble lead deposition on soil is immobilized by sorption on soil particles (Zimdahl, 1972) and is not subject to significant washoff. During the winter of 1971-1972, the Southern California Coastal Waters Research Project (SCCWRP, 1973) measured trace-metal concentrations in storm-water runoff flowing in the concrete-lined rivers, which act as storm sewers for the region. These rivers carry significant amounts of water only during storms. The samples were obtained by a depth-integrated method at various times throughout the storms. The chemical analysis included both the dissolved and particulate fractions for the metals. There was only one major storm during this period, however, and it is difficult to arrive at a firm number for the runoff input. Because a firm data base is lacking for this environmental pathway, a simple model for estimating the flux of runoff lead was developed. This model is discussed later in this Section. It is estimated from the model that approximately 140 tons/year is washed off the streets into the coastal waters during the rainy season (November-April). During the dry season, a small amount of water flows in the streets as a result of such domestic activities as lawn watering. Runoff during this season adds another 10 tons/year.

The final contributor to the anthropogenic lead burden of the coastal waters is the discharge of treated sewage in which the total lead emission rate is 230 tons/year or 0.64 tons/day (Parkhurst, 1973; City of Los Angeles, 1973; County Sanitation Districts of Orange County, 1973). The coastal water inputs are summarized in Table 8. The four "atmospheric" routes (dry deposition, rainout-washout, and dry-and wet-season runoff) account for more than 50 percent of the total, indicating that effective control of lead emissions to the coastal waters can be achieved only when both sewage and "atmospheric" routes are controlled. The runoff and sewage routes are essentially point sources of contaminants to the coastal waters whereas the deposition and rainout-washout routes act over a larger area of influence. It is likely that these two types of routes will have different ecological effects.

TABLE 8. INPUT OF ANTHROPOGENIC LOS ANGELES LEAD TO THE COASTAL WATERS

Input Route	Tons/Year	Tons/Day
Storm Runoff	140	0.4
Dry Deposition	120	0.3
Rainout-Washout	30	0.09
Dry Runoff	10	0.03
Municipal Sewage	230	0.64
TOTAL	530	1.46

Transport Of Windblown Lead Outside The Basin

To investigate the fate of the 5.6 tons/day of lead which is blown out of the Los Angeles Basin, the lead deposition was measured at four sites each in the San Gabriel-San Bernardino Mountains north of Los Angeles and in the Mojave Desert north of the mountains. The average deposition factors in these regions were 0.07 and 0.04, respectively, which are in general agreement with the factors calculated from the wild oats data (Rabinowitz, 1972) for the same regions. These factors, which are uncorrected for local sources, represent the maximum amount of Los Angeles lead depositing in these regions. If these deposition factors are applied to a 10,000-km^2 area corresponding to the mountain and desert part of the quadrant centered at northeast and extending approximately 150 km from downtown Los Angeles, a deposition flux of 0.2 tons/day is obtained. Although the source of this lead cannot be unequivocally attributed to Los Angeles, the general wind patterns and the sparse local traffic density strongly suggest Los Angeles as the source.

Directly to the east of Los Angeles is a semiurban region (Riverside-San Bernardino) comprising about 2,500 km^2 in area. Atmospheric lead concentrations measured at two sites in this region during the 1972-1973 ACHEX study were typical of lead concentrations in the Los Angeles urban area. From the previous discussion of lead deposition, the maximum deposition factor for Los Angeles lead in this region is equal to the average Los Angeles deposition factor. Maximum is specified because local sources, as opposed to lead blown out of Los Angeles, will also contribute to the deposition. This gives a flux of 1.1 tons/day. When the deposition in the mountains, deserts, and coastal waters is included, this accounts for only 1.7 out of the 5.6 tons/day which leaves Los Angeles. The difference, about 4 tons/day, is transported beyond a radius of 150 km from the city and exceeds the total lead emissions in the surrounding semiurban and nonurban areas as estimated on the basis of the respective motor vehicle populations and carbon monoxide emissions (State of California, 1972).

Roadway Deposition Of Lead And Runoff

The accumulation of lead in street dirt, the source of runoff lead, can be approximated by a simple differential equation:

$$\frac{dm}{dt} = Q - Rm \qquad (15)$$

the solution of which is:

$$m = \frac{Q}{R} + e^{-R\Delta t} \left(m_O - \frac{Q}{R}\right) \qquad (16)$$

where m is the mass of lead on the street, Q is the deposition rate minus the amount blown off the roads by wind, R is the fraction removed per unit of time by streetsweeping, Δt is the time in weeks since the last rainstorm, and m_O is the amount of lead remaining on the streets at the end of the last storm. Equation 16 is exact only when deposition and sweeping are continuous and constant with respect to time, but is sufficiently accurate for this analysis. The amount of lead washed off the streets is the product of m in equation 16 and the washoff efficiency, ε, which is a function of the rainfall intensity.

During the first major storm (December 21-22) of the 1971-72 rain season, 9.8 tons of lead washed off the Los Angeles River and Ballona Creek drainage basins (SCCWRP, 1973). These drainage basins account for 39 percent of the traffic density in the Los Angeles area and an extrapolation on the basis of traffic density to the whole Los Angeles area gives a washoff of 25 tons (Roberts et al., 1971). Because of the weak nature of the preceding storms, it is likely that the mass loading of lead on the streets prior to the December 21-22 storm was close to the steady-state value (Q/R in equation 16). Thus ε Q/R is equal to 25 tons.

Annual washoff can be estimated in the following manner. The rainy season in Los Angeles extends from November to April with 8 days of rainfall greater than 12 mm (U.S. Department of Commerce, 1968-1973) or an average of about one major storm per month. Actual rainfall patterns are complex and variable. For a model rain-year comprised of six major storms at 4-week intervals, Δt in equation 16 is 4 weeks for all storms except the first. Pitt and Amy (1973) found that the removal efficiency of lead by streetsweepers was 51 percent for a single pass. If the streetsweeping frequency is once per week, R is 0.51 per week. Using these values of R, Δt and $\varepsilon \frac{Q}{R}$ and neglecting m_O for all storms, we obtain a washoff in the first storm of 25 tons and in subsequent storms 22 tons per storm for a total of about 140 tons per year. This estimate is independent of Q/R and is only weakly dependent of R and m_0. The critical assumptions were the representative nature of the December 21 storm with respect to washoff efficiency and the extrapolation to area-wide runoff on the basis of traffic density. Considerable variations in the runoff lead-flux can occur however, and more data are needed to better describe this environmental pathway.

The deposition rate of lead on the streets can be estimated by setting the washoff efficiency for the December 21 storm to one. If, as assumed above, the streets are swept once a week with a 51 percent efficiency for lead removal, the roadway deposition rate is 1.8 tons/day or 660 tons/year. The remainder of the near deposition, 7.7 tons/day, deposits on the land adjoining the roadways. Because of the model dependency and the assumptions involved, these numbers must be regarded as approximate.

There is also a small runoff contribution during the dry season. We have measured the total lead content of dry weather runoff in the Ballona Creek drainage basin. If the result is extrapolated on the basis of traffic density to the whole urban area, a daily flow of 0.03 tons/day or 10 tons/year is obtained. The total input to the coastal waters via runoff is therefore 150 tons/year. The difference between the roadway deposition and the runoff flux is 510 tons/year or 1.4 tons/day. This is the amount removed by streetsweeping. In Los Angeles this lead is dumped in sanitary landfills and is immobilized in the same manner as soil lead.

Mass Balance for Automobile-Emitted Lead

The flow of automobile-emitted lead is summarized in Figure 11. In this flow diagram the flow rates are daily averages, i.e., the flow rates are the yearly fluxes divided by 365.

The mass balance constructed is shown in Table 9. The agreement between input and output routes is good. This mass balance applies to dry weather which is the situation for more than 90 percent of the days in Los Angeles.

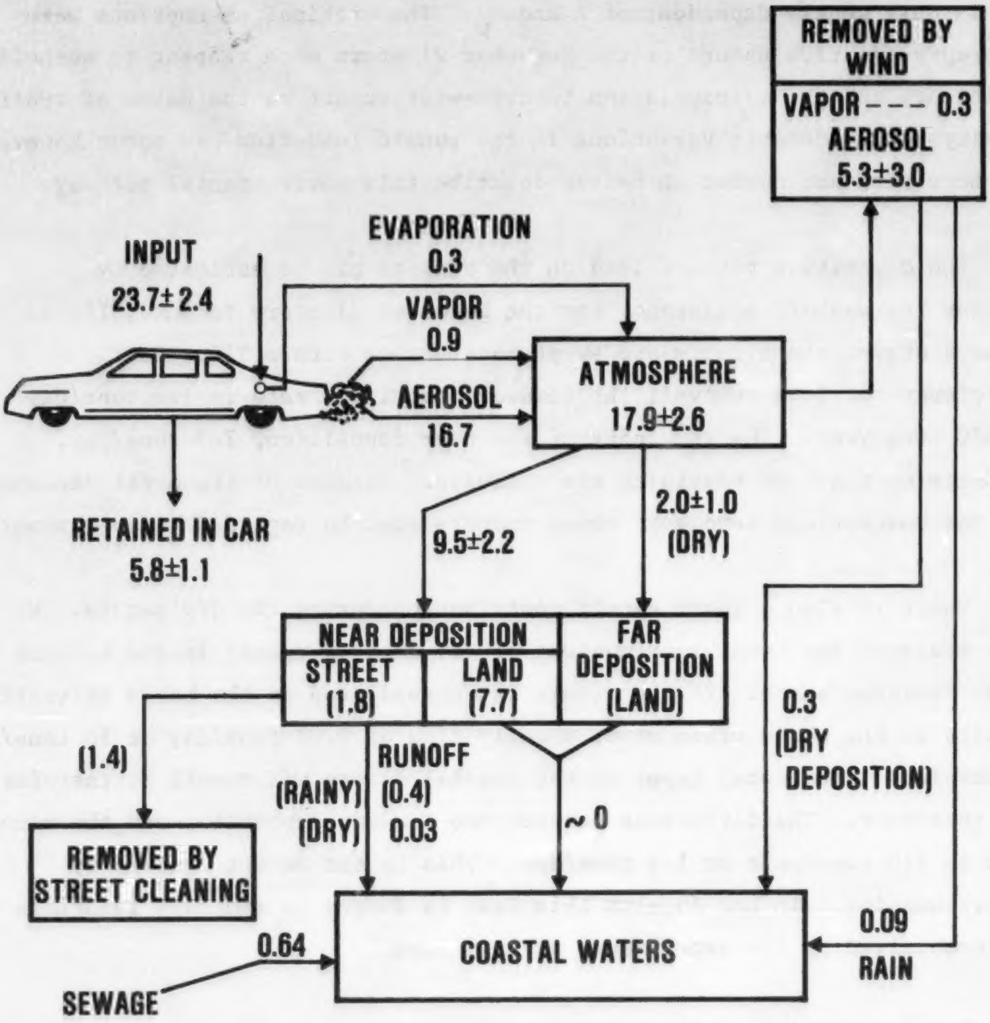
REMOVED BY WIND
VAPOR — — 0.3
AEROSOL 5.3±3.0
EVAPORATION 0.3
INPUT 23.7± 2.4
VAPOR 0.9
ATMOSPHERE 17.9±2.6
AEROSOL 16.7
2.0±1.0 (DRY)
9.5±2.2
RETAINED IN CAR 5.8±1.1
NEAR DEPOSITION
STREET (1.8)
LAND (7.7)
FAR DEPOSITION (LAND)
0.3 (DRY DEPOSITION)
(1.4)
RUNOFF
(RAINY) (0.4)
(DRY) 0.03
~0
REMOVED BY STREET CLEANING
0.64
COASTAL WATERS
0.09 RAIN
SEWAGE

Figure 11. The flow of automobile-emitted lead through the Los Angeles Basin (tons/day).

Because each of the output terms in the balance was independently derived, the agreement between input and output indicates that all major environmental pathways have been considered. This conclusion must be tempered, however, by the relatively large uncertainties in each of the terms. Improvements in the flow estimates will require better source characterization and a better theoretical and experimental understanding of particle removal processes.

TABLE 9. MASS BALANCE FOR AUTOMOBILE-EMITTED LEAD

Input (tons/day)		Output (tons/day)	
Evaporation of tetraethyl lead	0.3	Near Source Deposition	9.5 ± 2.2
Auto Exhaust (Aerosol 16.7) (Organic Vapor 0.9)	17.6 ± 2.6	Far Deposition	2.0 ± 1.0
		Removed by Wind (Aerosol 5.3) (Organic Vapor 0.3)	5.6 ± 3.0
	17.9 ± 2.6*		17.1 ± 3.9

*Inclusion of industrial emissions (0.3 tons/day) increases the total lead emissions to 18.2 tons/day.

The three output routes listed in Table 9 are not necessarily sinks. For example, lead which deposits on the streets can be washed off by rain into storm sewers which empty into the ocean, or lead which is blown out of the Los Angeles Basin serves as an input to other geographical regions. These secondary processes and their respective removal rates are shown on Figure 11.

Data for the rainout-washout of lead over the land area of the Los Angeles Basin are not available. Thus the values for far deposition and wind removal are for dry weather only. Of the 18 tons/day which is exhausted, approximately two-thirds of the lead is deposited within the Basin while the remaining one-third is blown out. Most of the lead which deposits on the land is immobilized in the soil, but that which settles on streets can be washed into storm sewers and ultimately into the coastal waters during the rainy season. The lead which remains airborne is primarily in submicron particles and can be transported well beyond the boundaries of the urban region. It must be borne in mind that large uncertainties do exist for both the input and output terms for the lead mass balance reported here.

THE LEAD IN THE SALINE BRANCH WATERSHED OF ILLINOIS

Another lead study was conducted by Rolfe and Haney (1975) for the Saline Branch Watershed. This watershed includes the Champaign-Urbana metropolitan area. The input of lead due to automobiles was determined according to the number of vehicle-miles traveled. Although a complete mass balance was not attempted, the ultimate fate of some of the lead entering the watershed was determined.

Gasoline consumption data were used in conjunction with estimates of the lead content of gasoline to arrive at 29 tons/year emitted. It has been estimated that 46 percent of the emitted lead remains airborne and is transported by winds out of the watershed. Thus 16 tons/year is deposited within the watershed. Of this, 14.3 tons/year is deposited either within the urban area which accounts for 12 square miles (19 square km) out of a total watershed area of 87 square miles (140 square km) or along major highways.

As a check on the above lead input calculations, dustfall measurements were made to determine the lead deposition at several locations in the watershed. The result was 9.5 tons/year as compared with the 16 tons/year estimated above. It is argued that the estimated value (16 tons/year) is more accurate because the dustfall measurements probably excluded some of the large material falling directly onto the roadway.

The only two significant exit pathways for lead from the watershed are through the air or via drainage waters. The air pathway has not been studied due to its complexity. The drainage waters have been examined, however, and the results show that only 7.5 percent of the 16 tons/year of lead deposited leaves the watershed. Most of the lead apparently accumulates within the watershed.

The major reservoirs of lead appear to be soil, vegetation, and stream sediments. Studies of animal life in the watershed show that a negligible fraction of the lead is contained in the wildlife. Although a mass balance has not been constructed, it has been demonstrated that a large fraction of the lead entering the watershed remains within it.

ATMOSPHERIC TRACE-METAL FLOWS IN THE LOS ANGELES BASIN: ZINC AND CADMIUM

In this example of mass balances, the methods developed for the analysis of the environmental flows of lead (Huntzicker et al., 1975a) are applied to zinc and cadmium. The emissions of each element exhausted into the atmosphere are quantified and the fate of these is traced through the environment. Estimates are made of the amounts of each element depositing over the land area of the Los Angeles Basin, advected out of the Basin, and entering the coastal waters. These estimates have important implications for control strategies. In the case of inputs to coastal waters the most important input route can be identified for each element. The amounts of these elements blown out of Los Angeles can be treated as primary inputs in emissions inventories for the downwind regions.

Trace Element Deposition Measurements

The experimental aspects of this work have been discussed in detail by Huntzicker et al. (1975a). Trace element deposition was determined on specially designed Teflon substrates, and particle size distributions were obtained with Andersen cascade impactors. Elemental analysis was by flame atomic absorption spectroscopy, although flameless, carbon rod atomic absorption was used in the later stages of the work.

Depostion of zinc and cadmium was measured in Pasadena for several periods between November 1972 and February 1974. A 1-week, synoptic measurement of deposition at six sites (including Pasadena) around the basin was made in July 1973. Deposition measurements were also made at four sites along the coast, and on Santa Catalina and San Clemente Islands. Deposition in Pasadena was simultaneously measured during the coastal measurement.

Atmospheric concentrations of zinc and cadmium were obtained during the 1972 and 1973 phases of the California Air Resources Board Aerosol Characterization Experiment (ACHEX) (Hidy, 1973). Carbon monoxide data were also obtained during ACHEX with Beckman GC 6800 air quality chromatographs. All uncertainties cited in this paper represent one standard deviation about the mean.

Zinc Emissions and Distribution

The major sources of atmospheric zinc in the Los Angeles area are metallurgical emissions, tire dust, and automobile exhaust. Metallurgical operations which are significant zinc emitters include secondary zinc melting, zinc sweating, zinc vaporization (distillation), brass melting, and iron and steel melting. In general, zinc is emitted as the oxide.

The percentages of zinc in the emissions from the different sources are summarized in Table 10. Total particulate emissions are about 450 kg/day from zinc operations in Los Angeles County and about 900 kg/day from brass melting (Thomas, 1974)*. The data in Table 10 show that the zinc content of these emissions is in the range 46 to 78 percent, which corresponds to zinc emissions of 600 to 1,100 kg/day. Total particulate emissions from iron and steel manufacturing in Los Angeles County are about 600 kg/day (Thomas, 1974)*. From the reported zinc composition of such emissions (Table 10), a zinc emission rate of 40 to 200 kg/day is obtained. Thus total metallurgical zinc emissions in Los Angeles County are in the range 600 to 1,300 kg/day. Orange County metallurgical emissions of all types are only about 7 percent of the Los Angeles County metallurgical emissions (State of California, 1972) and will not be included in this analysis.

---

* Thomas, G. Los Angeles County Air Pollution Control District, private communication (1974).

TABLE 10. ZINC CONTENT IN PARTICULATE EMISSIONS FROM METALLURGICAL OPERATIONS

Source	% Zn in Particulate Emissions	Reference
Zinc sweating	46	Herring (1971)
Red and yellow brass furnace (Los Angeles)	47	Allen et al. (1952)
Brass furnace	≤78	Danielson (1973)
Open hearth steel furnace	10-15	Danielson (1973)
Electric arc steel furnace	30	Danielson (1973)
Gray iron cupola furnace (baghouse sample)	6	Danielson (1973)

The zinc oxide aerosol which is formed during evaporation from molten zinc is generally in very small particles (< 0.3 μm) (Herring, 1971). Significant agglomeration apparently occurs, however, and the median diameter of the effluent zinc oxide is about 1 μm (Herring, 1971). Particulate matter emitted by steel melting is primarily (∿70 percent by weight) in the 0.10-μm size range but, in iron casting operations, only about 30 percent by weight of particulate effluent is in this size range (Danielson, 1973). It is not known, however, if the zinc particle size-distribution is the same as the total mass distribution.

Tire dust in the atmosphere has been studied in detail by Peirson and Brachaczek (1974). Pierson (1974) estimated that about 7.8 x 10^{-4} kg of tire dust is produced per vehicle mile or 1.1×10^{-4} kilogram per tire mile. (The "per vehicle mile" figure includes a 20 percent contribution from 18-wheel trucks.) Extrapolating 1969 traffic data by a 3 percent annual increase, approximately 1.3×10^{8} miles per day was driven in the Los Angeles area in 1973 (Roberts et al., 1971). Thus, production of 10^{5} kg/day of tire dust is estimated. Pierson and Brachaczek (1974) measured an average zinc content of 1.0 percent by weight for several different tire treads. The resultant production rate of tire dust is in very large particles (> 10 μm) with short atmospheric residence times (Pierson and Brachaczek, 1974; Dannis, 1974a; Raybold and Byerly, 1972).

Another major source of atmospheric zinc is automobile exhaust. This zinc most likely arises from the combustion of detergent lubricating oils which contain about 0.1 percent of zinc by weight (Pierson and Brachaczek, 1974; Ondov et al., 1974). Cahill and Feeney (1973) sampled freeway aerosols at several locations in Los Angeles and found that for particles less than 5 μm in aerodynamic diameter, the zinc-to-lead ratio is 0.013. This particle-size range excludes most of the tire dust zinc. Ondov et al. (1974) found a zinc-to-lead ratio of 0.012 for a tunnel study. Although size-distribution data were not given, this ratio probably corresponds to about the same size cutoff as the Cahill and Feeney ratio because of the 2-km length of the tunnel. The production rate of automobile exhaust zinc can be estimated from the Zn/Pb ratios given above, the emission rate (16,700 kg/day) of automobile exhaust particulate lead in Los Angeles (Huntzicker et al., 1975a) and the fraction of automobile exhaust lead in particles below the tire dust range. For reasons discussed below, 7 μm is the limit selected, although a cutoff of 5 μm would not significantly affect the result. For 40 percent of automobile exhaust lead in particles smaller than 7 μm (Habibi, 1973), the production rate of automobile exhaust zinc is 80 kg/day. Ninomiya et al. (1971) measured zinc automobile exhaust emissions of about 400 micrograms per mile averaged over ten Federal Test Procedure cycles. This corresponds to an emission rate of 50 kg/day for the Los Angeles area. Current measurements provide an estimate of the automobile exhaust zinc emission rate of 110 kg/day. This latter estimate is based on a freeway zinc concentration measurement of 0.48 $\mu g/m^3$ of which 0.37 $\mu g/m^3$ is attributable to automobile exhaust ($dp < 7$ μm), and lead concentrations of 14.1 $\mu g/m^3$ of which 12.0 $\mu g/m^3$ is automobile exhaust. Background concentration measurements from this study and from 1972-1973 ACHEX data indicate that 0.17 $\mu g/m^3$ of zinc and 2.2 $\mu g/m^3$ of lead are the background levels of automobile exhaust. Adjusting for these background levels, the ratio of zinc to lead in automobile exhaust at the freeway is 0.017. Applying this ratio to the 6.7 tons/day of the automobile emission estimate in the less than 7 μm range (Huntzicker et al., 1975a, and Habibi, 1973), the automobile zinc emission is calculated to be 110 kg/day. The average of the above three automobile zinc emission estimates is 80 kg/day.

The total atmospheric emissions of zinc in the Los Angeles Basin are 1,700 to 2,400 kg/day. Inputs from other sources such as the weathering of galvanized structures are presumed to be minor but are not known.

The fate of these atmospheric zinc emissions is removal by three major environmental pathways: "near" (source) deposition, "far" or basin-wide deposition, and advective (wind) removal.

To estimate the amount of airborne lead removed by wind from the Los Angeles Basin, carbon monixide was used as a mass tracer for airborne lead. While such an approach was acceptable for lead because lead and carbon monoxide are emitted from the same source, this method is less satisfactory for other species. The correct approach would involve a detailed, 3-dimensional mapping of pollutant concentrations and wind velocities as a function of time. Lacking such data, an estimate can be made using the carbon monoxide tracer method. In this application, carbon monoxide is not to be considered a tracer for zinc and other trace-metal pollutants, but rather a parameter which scales to the volumetric air flow through the Basin.

Values for zinc-to-carbon monoxide ratio (Zn/CO) at several sites in the Basin are given in Table 11; Zn/CO is 0.088 ± 0.041 $\mu m/m^3$/ppm or $(7.6 \pm 3.6) \times 10^{-5}$ as a dimensionless weight ratio. The Los Angeles

County Air Pollution Control District (MacBeth, 1974)* estimates that 6,450 metric tons/day of carbon monoxide was produced in the County by automobiles in 1973. Orange County adds another 20 percent (State of California, 1972) to bring the motor vehicle total to 7,700 tons/day. Stationary sources add an additional 4 percent (State of California, 1972) for a grand total of 8,000 tons/day for 1973. From Zn/CO we estimate that 600 ± 500 kg/day of zinc is blown out of the Basin.

TABLE 11. ZINC TO CO AND CADMIUM TO CO RATIOS IN THE LOS ANGELES BASIN

Site	ZN/CO $g/m^3/ppm$	Cd/CO $g/m^3/ppm$
Pasadena	0.032	0.002
West Covina	0.089	0.002
Rubidoux	0.089	0.004
Dominguez Hills	0.15	0.003
Pomona	0.076	0.001
Average	0.087 ± 0.041	0.002 ± 0.001

The near deposition of zinc can be estimated from source and receptor particle size-distributions as was the case for lead. Particle size-distributions at a Los Angeles freeway and in Pasadena, a typical receptor site, are shown in Figure 12. The dashed lines assume that the smallest particle size is 0.01 μm and the largest 50 μm. The freeway distribution shows considerably more mass above 7 microns than the Pasadena data. This shows that much of the airborne tiredust zinc deposits near the source. It should be cautioned, however, that these impactor runs were nonisokinetic and, therefore, the concentration of large particles is underestimated. It is still possible, however, to use the data to determine an upper limit for near deposition.

---

* MacBeth, W., Los Angeles County Air Pollution Control District, private communication (1974).

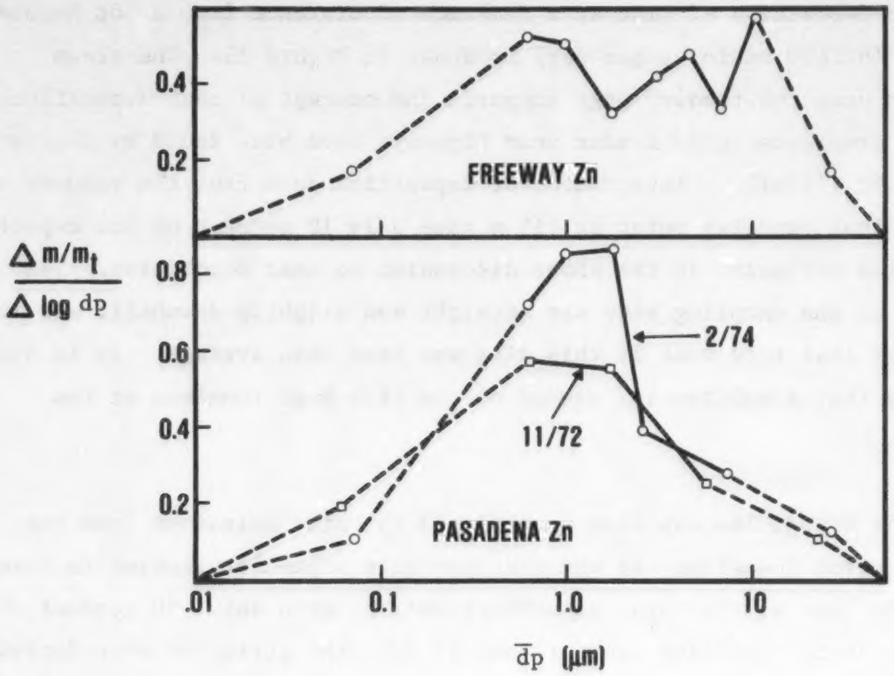

Figure 12. Differential mass distributions for zinc at 1 meter from a freeway and for Pasadena.

According to the Pasadena distribution, abcut 14 percent of the zinc mass is greater than 7 microns. If this distribution is typical of zinc particle size-distributions around the Basin, then about 80 kg/day (14 percent of 600 kg) is blown away from the roadway. The remainder of the tire dust zinc, 920 kg/day, is assumed to have a short atmospheric residence time and to deposit on or near the roadways. Because 80 kg/day is a lower limit for zinc blown away from the roadway, 920 kg/day is an upper limit for near deposition.

The deposition of zinc as a function of distance from a Los Angeles freeway (62,000 vehicles per day) is shown in Figure 13. The steep gradient near the roadway edge supports the concept of near deposition. Similar gradients in soil zinc near highways have been found by Lagerwerff and Specht (1970). Integration of deposition data from the roadway edge to the final sampling point at 115 m gave only 10 percent of the expected deposition estimated in the above discussion on near deposition. The roadway at the sampling site was straight and slightly downhill, and it is likely that tire wear at this site was less than average. It is also rossible that a substantial amount of the tire dust remained on the roadway.

Near deposition can also be expected for zinc emissions from the ferrous metal industry. If the zinc particle size-distribution is assumed to be the same as the total mass distribution, then about 50 percent of the zinc is in particles greater than 10 μm. The estimated near deposition of zinc is then about 60 kg/day.

Measurements of zinc deposition at Pasadena and other receptor site locations around the Basin can be used to evaluate the far deposition component. The average Pasadena deposition for ten periods between November 1972 and February 1974 was 14 ± 3 ng/cm^2/day. For the basin-wide synoptic measurement, the average deposition normalized to Pasadena was 1.1 ± 0.6. This gives an average zinc deposition flux for the Los Angeles Basin of 15 ± 9 ng/cm^2/day. For an area of 4,430 km^2 the basin-wide deposition is 660 ± 390 kg/day. This probably represents a lower limit for surface deposition because it is based on the superficial area of the Basin. More data are needed to evaluate the effects of vegetation and man-made structures.

A mass balance for Los Angeles zinc is shown in Table 12. The output flows are for dry weather which accounts for more than 90 percent of the days in Los Angeles. Although the overall agreement is satisfactory the limits of error are large, and it is possible that unidentified

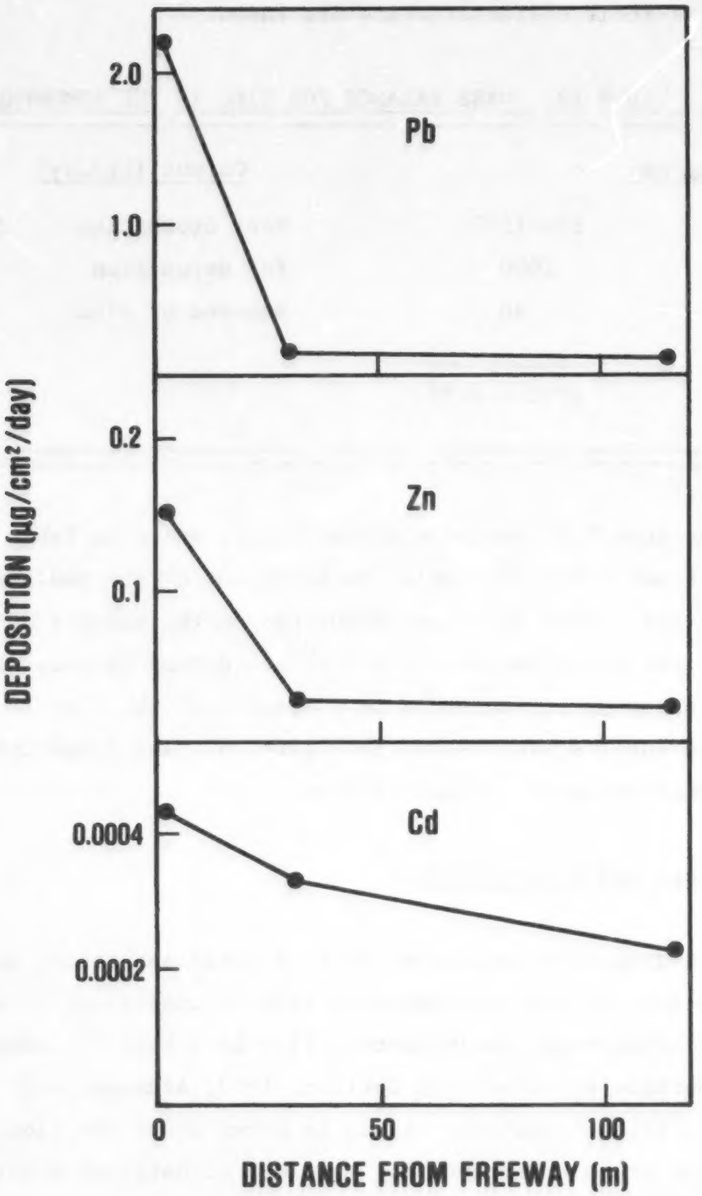

Figure 13. Deposition as a function of distance from a freeway for Pb, Zn, and Cd.

sources exist. The environmental significance of such sources can only be determined if their characteristics are known.

TABLE 12. MASS BALANCE FOR ZINC IN THE ATMOSPHERE

Input (kg/day		Output (kg/day)	
Metallurgical	600-1300	Near deposition	≲ 980
Tire dust	1000	Far deposition	660 ± 390
Auto exhaust	80	Removed by wind	600 ± 500
	1700 - 2400		∿ 2200

As was the case for lead, the output routes shown in Table 12 are not final sinks. Some of the zinc which is blown out of the Basin can deposit on the coastal waters. Zinc which has deposited on the streets and the land can be washed into storm sewers and out to sea during rainstorms. These environmental pathways are included in a diagram of the flow of zinc through the Los Angeles Basin shown in Figure 14. The flows into coastal waters are discussed later in this Section.

Cadmium Emissions and Distribution

Cadmium is generally considered to be a toxic substance, and consequently a knowledge of its environmental flow is important. Its toxic properties and broad-scale environmental flow have been reviewed in considerable detail (Fulkerson and Goeller, 1973; Athanassiadis, 1969; Friberg et al., 1971). However, little is known about the flow of cadmium through specific urban environments. The lack of detailed emission inventories has been the primary obstacle. The Los Angeles area is no exception.

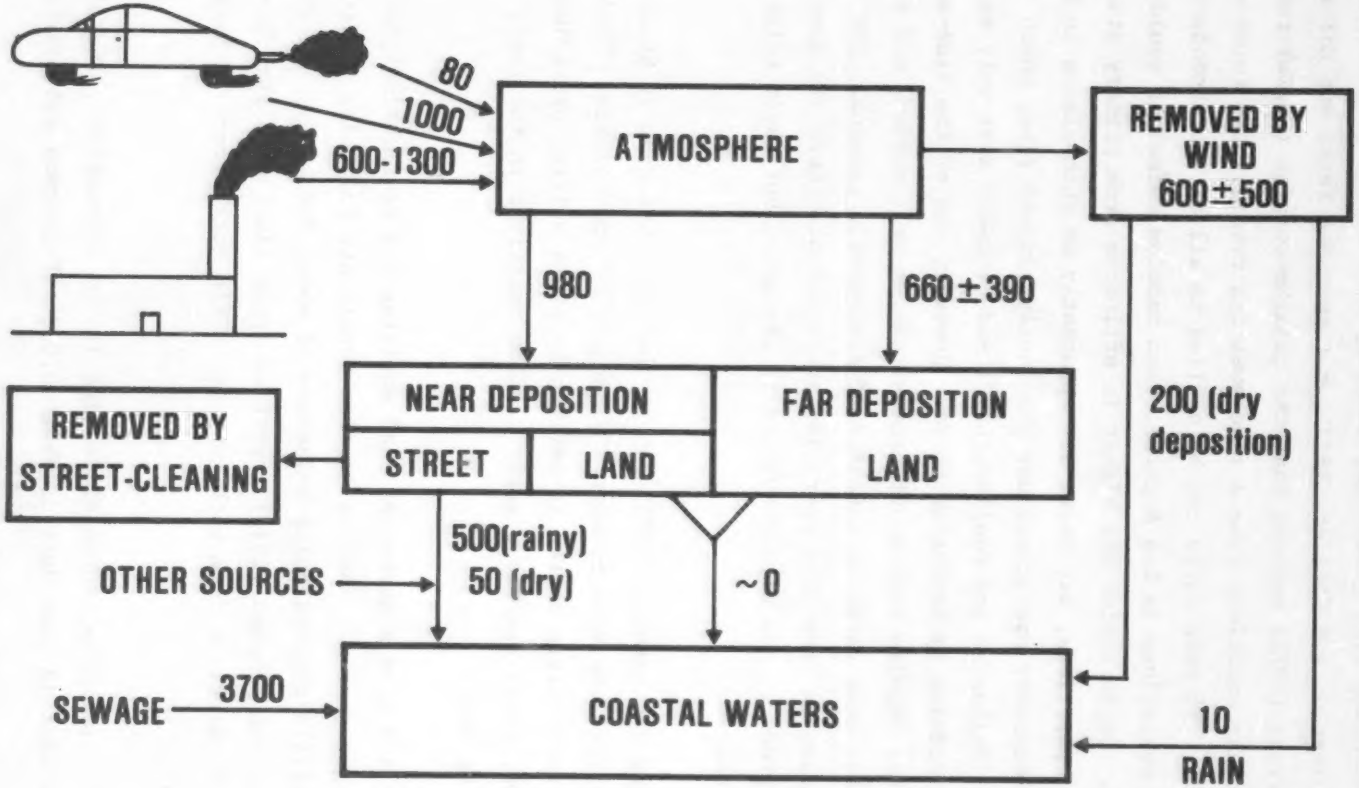
80
1000
600-1300
ATMOSPHERE
REMOVED BY WIND 600±500
980
660±390
NEAR DEPOSITION
STREET
LAND
FAR DEPOSITION
LAND
REMOVED BY STREET-CLEANING
200 (dry deposition)
500(rainy)
50 (dry)
OTHER SOURCES
~0
SEWAGE
3700
COASTAL WATERS
10
RAIN

Figure 14. Zinc fluxes in the Los Angeles Basin kg/day/(average)

The secondary zinc processing industry is a source of atmospheric cadmium (Fulkerson and Goeller, 1973), but emission rates are not well known. Herring (1971) reports that the cadmium-to-zinc (Cd/Zn) ratio for particulate emissions from a zinc-sweating reverbertory furnace was about 0.0006. If this ratio can be applied to all of the secondary zinc processing operations in Los Angeles, then cadmium emissions would be about 0.6 kg/day. Cd/Zn ratios are higher in effluents from primary zinc processing operations, but there are apparently no such plants in Los Angeles. Secondary operations use previously refined zinc, which is low in cadmium (Fulkerson and Goeller, 1973) and probably emit only small amounts of cadmium as indicated above. However, one of the zinc-smelting plants in Los Angeles also manufactures cadmium ball anodes, and it is possible that this could be a source of atmospheric cadmium. The particulate cadmium emissions from this operation are unknown. There are also a number of plants producing cadmium chemicals in the area, but their emissions are also unknown.

Lee and von Lehmden (1973) report that baghouse dust in brass and bronze smelters contains between 100 and 10,000 ppm cadmium. Since 910 kg/day of particulate matter is emitted by brass melting operations in Los Angeles, these fractions imply cadmium emissions in the range 0.09 to 9 kg/day.

There are also a number of lead smelting and fabricating plants in the Los Angeles area. The Los Angeles County Air Pollution Control District (Thomas, 1974)* reports daily emissions of about 300 kg/day for these plants, but Lee and von Lehmden (1973) report an upper limit of 1 ppm cadmium in particulate emissions from such sources. This corresponds to less than 0.3 kg/day.

Another possible source of cadmium is the automobile. The ratio of cadmium to zinc in tire dust is about 0.0006 (Fulkerson and Goeller, 1973;

---

* Thomas, G., Los Angeles County Air Pollution Control District, private communication (1974).

Pierson, 1974)* which corresponds to an emission rate of 0.6 kg/day. As noted above, most of this will deposit on or near roadways. An analysis of three motor oils and twelve brands of gasoline gave cadmium concentrations of about 0.2 ppm for the former and less than 0.01 ppm for the latter (Lagerwerff and Specht, 1970). The resultant automotive cadmium emission is less than 1 kg/day.

All of these emission sources add up to a few kilograms per day at most. The Los Angeles County Air Pollution Control District estimates an emission rate of less than 40 kg/day. As will be seen below, at least 20 kg/day is necessary to satisfy the measured environmental flows.

Values of cadmium to carbon monoxide ratio (Cd/CO) at several sites in the Basin are given in Table 11. From the average value of Cd/CO = 0.002 ± 0.001 $\mu g/m^3/ppm$, an estimate of 14 ± 10 kg/day of cadmium is advected from the Basin by wind. The average deposition flux for five different measurement periods in Pasadena was 0.13 ± 0.07 $ng/cm^2/day$. Because cadmium data were obtained during the urban synoptic measurements, basin-wide (far) deposition is based on the Pasadena deposition. This estimate is 6 ± 3 kg/day.

The deposition of cadmium as a function of distance from a freeway is shown in Figure 13. Similar gradients for cadmium in roadside soil and vegetation have been reported by Lagerwerff and Specht (1970). The gradient is much weaker than the corresponding zinc profile, but a factor of two difference, between the 1 m and 115 m points, still exists. Integration between the roadway and the 115 m point (assuming that the latter point represents "background") gives an emission rate of about 3 μg per car mile or 0.4 kg/day for the whole Basin. This is almost 70 percent of the amount expected from tire dust. Because zinc deposition at the same location account for only about 10 percent of the amount expected from tire dust, the existence of other automotive sources may be indicated.

---

* Pierson, D.H., Private communication (1974).

The input and output flows are summarized in Table 13. The known sources account for (at most) one-half of the environmental flow and it is impossible to judge whether all of the cadmium emitted into the atmosphere has been accounted for. Clearly better emissions data are required.

TABLE 13. MASS BALANCE FOR CADMIUM IN THE ATMOSPHERE

Input (kg/day)		Output (kg/day)	
Secondary zinc processing	0.6	Near (roadway) deposition	0.4
Cadmium processing	?	Far deposition	6 ± 3
Brass melting	0.09 to 9	Removed by wind	14 ± 10
Lead smelting	0.3		
Tire dust	0.6		
Auto exhaust	< 1.0		
	3 - 11		20 ± 13

Trace-Metal Inputs to the Coastal Waters

Trace metals can enter the coastal waters by at least six routes: dry atmospheric deposition, rainout-washout, rainy season runoff, dry season runoff, discharge of treated wastewaters, and discharge of untreated wastes. Estimates based on available information for all of these routes can be made except for the discharge of untreated wastes. Analyses will depend heavily on work discussed earlier on automobile-emitted lead to the coastal waters (Huntzicker et al., 1975b).

The deposition of lead, zinc, and cadmium normalized to their respective coastal values are plotted as a function of distance from the coastal baseline in Figure 15. The solid line is an extrapolation to the coast, and the dashed line represents "background" or contribution from non-Los Angeles lead deposition (Huntzicker et al., 1975b). The open symbols represent 1973; filled symbols represent 1974. The average coastal deposition values are: lead, 10 ng/cm^2/day, zinc, 7.6 ng/cm^2/day and cadmium, 0.12 ng/cm^2/day. These values are based on measurements conducted for this analysis and do not average in deposition flux data reported by others.

Zn/Pb ratios for several locations are listed in Table 14. The difference between the inland air and inland deposition ratios can be attributed to different particle size-distributions for lead and zinc. Large enrichments of zinc relative to lead are observed for Catalina rain (Lazrus, et al., 1970) and for sediments in Santa Barbara, Santa Monica, and San Pedro marine basins (Bruland et al., 1974). Lazrus' data were

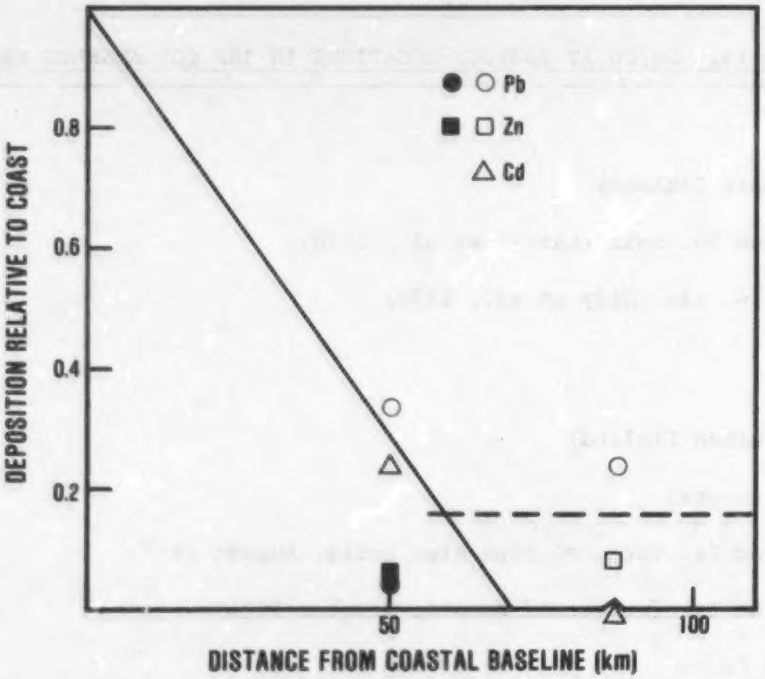

Figure 15. Deposition of Pb, Zn, and Cd as a function of distance from the coast.

obtained at the Catalina airport weather station which is near a zinc mine; this may have influenced his data. The sediments are probably influenced by the large amounts of zinc present in the sewage effluents and storm water runoff which are discharged into the coastal waters.

Smaller enrichments of zinc are seen in coastal deposition with respect to inland deposition and in San Nicolas Island air with respect to inland air (Hidy et al., 1974). The enrichment in coastal deposition cannot be attributed to zinc in windblown sand because an insufficient amount of sand on the deposition collector was observed. It is possible that industrial sources located along the coast are responsible. In Table 15 the ratios of coastal deposition to inland deposition and Catalina deposition to inland deposition are given for lead, zinc, and cadmium. Although the uncertainties are large, the smallest ratio in both cases was

TABLE 14. Zn/Pb AT VARIOUS LOCATIONS IN THE LOS ANGELES AREA

Airborne	Zn/Pb Ratio
Los Angeles air (inland)	0.12
Santa Catalina Is. rain (Lazrus et al., 1970)	2.60
San Nicolas Is. air (Hidy et al., 1974)	0.50
Deposition	
Los Angeles urban (inland)	0.33
Los Angeles coastal	0.75
Santa Catalina Is. (area of high zinc soils, August 1973)	5.50
Santa Catalina Is. (relocated sample, October 1974)	0.85
San Clemente Is.	0.25
Marine	
Storm runoff (December 21, 22, 1972)	1.4

(Continued)

TABLE 14. Zn/Pb AT VARIOUS LOCATIONS IN THE LOS ANGELES AREA (Continued)

Airborne	Zn/Pb Ratio
Dry weather runoff (July 1973)	0.7
Sediment accumulation rates (Bruland et al., 1974)	3.9
(natural)*	11.0
(anthropogenic)	1.5
Sewage effluent	5.7
Miscellaneous	
Santa Monica sand (25 ppm Zn)	1.6

* determined from pre-1920 sediments

observed for lead for which most of the emissions are inland. Larger ratios were observed for zinc and cadmium; this is consistent with the fact that some stationary sources are located along the coast.

TABLE 15. DEPOSITION RATIOS, AUGUST 1973

	Coastal Inland	Santa Catalina Inland
Pb	0.2 ± 0.1	0.07 (Oct. 1974 0.008)
Zn	0.5 ± 0.4	0.80 (Oct. 1974 0.02)
Cd	0.9 ± 0.7	0.22

The factor of 9 decrease in Catalina to inland lead deposition between the August 1973 and October 1974 experiments may have resulted from differences in meteorology during the two experiments. However, the equivalent ratio for zinc shows a factor of 40 decrease. This may have been caused by changes in meteorology and by the lower zinc content of the soil at the location of the October 1974 run.

The atmospheric deposition of cadmium on the coastal waters is estimated by assuming that the deposition decreases linearly between the coast and Catalina (solid straight line in Figure 15). This defines an area of influence of Los Angeles which extends to about 70 km from the shore and gives an area of 5600 km^2 for an 80 km long coastline. The resultant cadmium deposition flux to this coastal region is 3.5 kg per day. The input of Los Angeles zinc to the coastal waters is assumed to fall along the solid line in Figure 15. The resultant flux is 200 kg/day. No corrections for non-Los Angeles background were made as in the lead analysis. On an annual basis,* the inputs are 70 tons/year of zinc and 1 ton/year of cadmium.

The rainfall fluxes of Los Angeles zinc and cadmium are estimated from the rainfall flux of lead (30 tons/year) and the ratios of airborne Zn/Pb and Cd/Pb (0.12 and 0.004, respectively) in Los Angeles air. Thus approximately 4 tons/year of zinc and 0.1 tons/year of cadmium enter this coastal water region by rainout-washout. As noted earlier the region of influence of Los Angeles with respect to rainout-washout may be larger than the region of influence for dry deposition, but to confirm this requires additional data that are not currently available.

To estimate the amount of lead entering the coastal waters by runoff in the rainy season, Huntzicker et al. (1975b) developed a simple model based on measured runoff fluxes for a storm on December 21, 1971 and several assumptions concerning the accumulation and removal rates of lead in street dirt. By scaling the model-dependent lead flux (140 tons/year) by the ratios Zn/Pb (1.4) and Cd/Pb (0.01), for the December 21, 1971 storm, zinc and cadmium runoff fluxes can be estimated. These runoff fluxes are 170 tons/year for zinc and 1 ton/year for cadmium. As was the case for lead, more data are needed to better define these fluxes.

---

* There is an average of 19 days per year in the Los Angeles region in which the total rainfall is greater than 2.5 mm (U.S. Department of Commerce, 1968-1973). A "dry" day is defined as one for which the total rainfall was less than 2.5 mm, and the coastal water deposition fluxes are calculated on the basis of 346 dry days per year.

The zinc runoff of about 500 kg/day is more than half of the estimated near deposition. The application of the lead runoff model to zinc implied an accumulation rate of zinc in street dirt of more than twice the estimate for near deposition of zinc. However, Pitt and Amy (1973) found that the average loading of zinc in street dirt for several American cities was only about one-fourth of the loading of lead. Thus, a substantial fraction of runoff zinc probably comes from non-street dirt, nonautomotive sources (e.g., corrosion of galvanized structures).

The trace-metal inputs from runoff during the dry season can be estimated from runoff fluxes in the Ballona Creek drainage basin. From a sample taken in August 1973 the estimated flows to the drainage basin are 2.4 kg/day for zinc and 0.1 kg/day for cadmium. The Ballona Creek drainage basin constitutes 5 percent of the area of the Los Angeles study region. An extrapolation on the basis of area to the whole region gives dry runoff fluxes of 20 tons/year for zinc and 0.7 tons/year for cadmium.

Trace metals also enter the coastal waters in sewage effluents. These fluxes are 1,300 tons/year of zinc and 27 tons/year of cadmium (Parkhurst, 1973; City of Los Angeles, 1973; and County Sanitation Districts of Orange County, 1973). In Table 16 the trace-metal flows for all the environmental pathways into the coastal water are summarized. Despite substantial uncertainty in these estimates, it is clear that sewage effluent is the dominant input for zinc and cadmium, and that control strategies for these elements should focus on the sewage route. In the case of lead, however, the "atmospheric" routes (including runoff) are important and must be considered in a coastal water lead-control strategy.

TABLE 16. ANTHROPOGENIC INPUTS OF LOS ANGELES Pb, Zn, AND Cd TO THE COASTAL WATERS

	Tons/Year		
Input Route	Pb	Zn	Cd
Storm runoff	140	170	1
Dry deposition	120	70	1
Rainout-washout	30	4	1
Dry runoff	10	20	0.07
Municipal sewage	230	1300	27

SECTION V

TRANSPORT AND DEPOSITION THROUGH THE WATER ROUTE

FLOWS OF ARSENIC IN THE SOUTHERN CALIFORNIA WATER ENVIRONMENT

Arsenic enters the Southern California coastal basin in stream flows, ground waters, water supply aqueducts, atmospheric transport, and in the form of raw materials and manufactured goods. It is discharged to the coastal waters in stream flows and in domestic-industrial wastewater effluents (liquid and solid). Arsenic accumulates in coastal sediments in the vicinity of wastewater discharges. Arsenic is also added to the land as sludges recovered from municipal wastewater processing. Atmospheric emissions within the basin may be deposited on the land or on the coastal waters, or transported from the basin by prevailing winds. However, recent information on arsenic emissions to the atmosphere or on ambient air concentrations of arsenic in the Los Angeles Basin have not been identified.

A preliminary assessment of arsenic flows in the Southern California water environment can be made through an examination of water quality and hydrologic data of the U.S. Geological Survey, influent and effluent wastewater characteristics reported by the County Sanitation Districts of Los Angeles and the City of Los Angeles, and reports of the Southern California Coastal Water Research Project (SCCWRP) on mass emissions of metals.

The mean annual runoff of rivers discharging to the Southern California Bight is about 600 million m^3/year (SCCWRP, 1973). Mean daily runoff is highly variable during storm periods. On twelve dates in the period from February 6, 1973, through October 20, 1975, the Geological Survey measured arsenic in samples from the Los Angeles River at Long Beach (U.S. Geological Survey, 1973). Total arsenic concentrations in the twelve samples ranged from 3 to 26 µg/l; mean daily discharges for the twelve sampling dates varied from 0.6 to 60 m^3/sec. The U. S. Geological Survey data reveal that arsenic is present in both particulate and dissolved fractions in most Southern California river water. Since the flow and arsenic concentration are uncorrelated, the annual flux may be estimated as the product of the annual flow of the Los Angeles River (150 x 10^6 m^3/year) and the mean concentration (10 µg/l), or 1.5 tons/year.

Since the mean annual runoff of the Los Angeles River is about 25 percent of the total annual stream discharge to the bight, a rough estimate of the total arsenic flux to the bight from all streams, based on the Los Angeles River data, is about 6 tons/year.

An alternative approach is to select an average arsenic concentration for the thirty individual analytical results for the three rivers sampled--Los Angeles River, Santa Clara River, and Santa Ana River-- and to estimate a typical annual flux as the product of the average concentration and the mean annual runoff for the entire Southern California Bight. The mean of thirty total arsenic values for the three rivers (1973-75) is 7 µg/l. The typical river flux to the entire bight is then estimated about 4 tons/year.

The discharge of municipal wastewaters to the Southern California Bight totaled 1,431 million m^3/year in 1974 (SCCWRP, 1975). The total mass emission rate (flux) for arsenic from all municipal waste discharges was estimated by SCCWRP to be greater than 21 tons/year in 1974. The dominant discharges of arsenic are from the Los Angeles County Joint Water Pollution Control Plant (JWPCP) outfalls off Palos Verde (11.3 tons/year), the City of Los Angeles (Hyperion) final effluent to Santa Monica Bay (4.7 tons/year), the sludge line to Santa Monica Canyon (1.2 tons/year), and the San Diego outfall at Point Loma (greater than 3.7

tons/year). Arsenic data have not been reported for the Orange County outfall (flow of 236 million m^3/year).

Arsenic entering the Hyperion treatment plant in the 1971-1972 period was estimated at 4.1 tons/year from domestic waste and about 1 ton/year from industrial waste (City of Los Angeles, 1973), or 81 percent from domestic and 19 percent from industrial sources. These are the same proportions for the wastewater flow. Measured concentrations did not reflect quality differences between residential and industrial wastewaters with respect to arsenic. The City of Los Angeles has identified industrial processes which produce products which contribute to the arsenic mass flux at Hyperion. These are flue dust of lead and copper smelting, hardening lead shots, copper alloys, lead base alloys for battery grids, bearings, cable sheaths, anodes, high-temperature brasses, copper alloy tubes, dental amalgams, solders, and pesticides (City of Los Angeles, 1973). The Sanitation Districts of Los Angeles County have identified the following types of industry as emitting arsenic to the sewer system: blast furnaces and mills, ferrous foundries, nonferrous foundries, and apparel (City of Los Angeles, 1973). From the data reported by the City of Los Angeles for 1971-1972, 7.1 tons/year arsenic is estimated in Hyperion plant influent. This corresponds to a concentration of 15 μg/l in a mean flow of 344 million gallons per day (MGD) (475 million m^3/year). This estimate is not very reliable because of the low number of analyses for arsenic. The weighted-water-supply source contribution of arsenic to Hyperion flow for 1971-1972 is estimated at 6.7 tons/year, based on treatment plant flows and concentrations reported for the Owens River aqueduct, groundwater, and Colorado River water (City of Los Angeles, 1973). Total arsenic emissions from Hyperion (effluent plus sludge outfalls) for the years 1971, 1973, 1974, and 1975 have been estimated by SCCWRP to be 3.5, 7.4, 5.9, and 4.8 tons/year, respectively (SCCWRP, 1974, 1975, 1976). There is reason to believe that the 1971 data for arsenic are not reliable because of the insufficient sensitivity of earlier analytical methods (SCCWRP, 1974).

The arsenic content of sludge solids discharged through the Hyperion 7-mile outfall (arsenic flux, 1 to 2 tons/year) can be estimated from data on the total suspended solids concentration and total arsenic concentration of the sludge, assuming that all arsenic is in the sludge particulates. The average arsenic concentration of the sludge in 1974 was 0.18 mg/l, and the average suspended solids concentration was 7,300 mg/l. The arsenic content of the sludge solids is then estimated at 25 mg/kg as an upper limit. Observations on arsenic contents of bottom sediments in the vicinity of the 7-mile outfall (City of Los Angeles, 1973) show accumulations of perhaps 2 to 3 times background levels.

Arsenic flows at the JWPCP of the County Sanitation Districts of Los Angeles (discharged to the ocean at White's Point) appear to have increased from 1970 through 1974, but this may be only a reflection of the unreliability of earlier analytical results for arsenic (data frequently reported as 0.01 mg/l). Arsenic flows at the JWPCP have been estimated as follows:

Flow	Ton/Year	Reference
From Water Supply (1970)	< 4.5	Sanitation Districts of Los Angeles County, 1973
Influent (1971)	< 5.3	Sanitation Districts of Los Angeles County, 1973
Effluent		
(1973)	7.4	SCCWRP, 1975
(1974)	11.3	SCCWRP, 1974
(1975)	5.2	SCCWRP, 1976

The 1974 JWPCP arsenic flow to the ocean represents a total arsenic concentration of 25 μg/l in a wastewater flow of 346 million gallons per day (477 million m^3/year).

Arsenic concentrations in seawater are reported to range from 0.8 to 8.0 μg/l, with a representative total concentration of 3.7 μg/l (Brewer, 1975).

In these data, the advective transport of arsenic through the Southern California Bight (surface area 1×10^{11} m^2, mean depth of surface mixed zone 50 m, residence time 3 months) is about 70,000 tons/year. The ratio of total arsenic concentration in JWPCP effluent to typical arsenic concentration in seawater is 25 to 3.7, or 6.8. Dilution of 1 part of effluent with 100 parts of seawater results in an arsenic concentration in the mixture of 3.9 µg/l, or an increment over background of 0.2 µg/l.

Typical concentration ranges for arsenic in waters, wastewaters, sludges, and sediments in Southern California are as follows:

	Arsenic Concentrations
Water Supplies	< 10 to 30 µg/l
Stream Flows	1 to 26 µg/l 7 µg/l (mean)
Wastewater Effluents	10 to 30 µg/l
Wastewater Sludges	150 to 300 µg/l (sludge) 15 to 30 mg/kg (solids)
Marine Sediments (background)	1 mg/kg
Marine Sediments & Sludge (near outfalls)	4 to 9 mg/kg

Estimated typical arsenic total flows in the Southern California environment are as follows:

	Metric Tons Per Year
Streams	4 to 6 (1973-75)
Wastewater Effluents	18 to 20 (1974), 10 (1975)
Wastewater Sludges	1 to 2 (1974), 2 (1975)
California Bight Advection	70,000

Arsenic flows in Southern California wastewater effluents for 1975 have recently been summarized by SCCWRP (1976). The total mass emission of arsenic to the bight, exclusive of Orange County effluent, was estimated to be 12 tons/year. A major decrease from 11.3 to 5.2 tons/year in comparison to 1974 data is reported for the JWPCP (Los Angeles County) effluent. The Point Loma discharge (San Diego) of arsenic decreased from more than 3.73 to 0.15 tons/year. These changes probably reflect improved analytical methods for arsenic. Source control programs may also have influenced effluent levels of arsenic.

On the basis of this preliminary assessment it appears that wastewater effluents are the dominant water transport influence in increased arsenic fluxes to the coastal waters. With expected seawater-to-wastewater dilution ratios on the order of 100:1, a concentration increase above background in the water column of less than 5 percent should result. Increases of 5-to 10-fold in arsenic content of coastal sediments are experienced in the immediate vicinity of outfalls in Santa Monica Bay, reflecting accumulation of arsenic-containing sludge solids and effluent particulates.

Data on atmospheric emissions and ambient air concentrations of arsenic in Los Angeles are needed to complete the mass balance assessment of arsenic in the Los Angeles Basin.

THE ULTIMATE FATE OF SEWAGE PARTICULATE MATTER

Many studies have been conducted involving simultaneous diffusion and sedimentation of particles during long-term transport from the source. These studies have involved particles in both air and water.

Considerable meteorological data are available on wind and temperature profiles, and on the nature of atmospheric turbulence. These data are useful in validating the modeling of transport processes in the atmosphere. A different situation exists for the long-term transport of particles in bodies of water where current data are scarce. Of the many studies involving particle behavior in oceans, for example, few have attempted to incorporate actual ocean current data and turbulence characteristics into the various models.

A study has been conducted concerning the physical behavior of particles from ocean outfalls. The object of this study was to determine where sewage or sludge particles eventually come to rest on the ocean floor after being discharged from a submarine outfall diffuser pipe. The relevant parameters considered include the size, distribution, and densities (hence settling velocities) of emitted particles, the ocean currents, the structure of the ocean bottom, the temperature and salinity of the ocean water, and the composition of the effluent sewage. Given appropriate values for these parameters, it is possible to use the models developed by Koh* to predict the eventual "fallout distributions" of the ocean bottom. A brief summary of the methodology used in making these predictions is presented here.

Typical submarine outfalls discharge treated effluent several kilometers from shore through diffuser pipes on the ocean bottom, usually at depths of about 60 m on the West Coast. The effluents contain some fine particles not removed in the treatment. Furthermore, some digested sludge particles may either be added back in the effluent stream or discharged through a separate small sludge outfall.

After being discharged into the ocean, the wastewater plume rises until reaching density equilibrium. The wastewater has a density slightly less than the surrounding seawater. This density difference drives the initial plume rise. The temperature and salinity structure of the ocean, as well as currents, then control the extent to which the plume rises.

---

* Koh, R. C. Y., "Physical Disposition of Particulates from Ocean Outfalls," Report to the Environmental Protection Agency, W. M. Keck Laboratory of Hydraulics and Water Resources, Pasadena, California, (in preparation).

The plume rise occurs over relatively short time scales, on the order of minutes or tens of minutes. Because the sedimentation velocities of the sewage particles are small (10^{-5} to 10^{-2} cm/sec), their fall distance over the time scale of the plume rise is negligible compared to that of the plume rise itself. It may therefore be assumed that the particle settling does not begin until after the plume has found its equilibrium position. The concentration distribution of sewage particles after the plume rise has ceased represents the initial condition for the following models.

Model 1: Differential Equation Approach

The idea behind this model is to obtain a numerical solution to the steady advective diffusion equation representing the transport processes after the initial plume rise. Particle coagulation and exchange with the surrounding fluid are not taken into account. The equation and boundary conditions pose a boundary value problem which may be solved using a digital computer. The basic equation for a collection of particles with sedimentation velocity v_s is:

$$u(z)\frac{\partial c}{\partial x} - v_s \frac{\partial c}{\partial z} = \frac{\partial}{\partial y}\left(K_y(y)\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z(z)\frac{\partial c}{\partial z}\right) \qquad (17)$$

where the x-axis is parallel to the ocean current, y is the transverse coordinate, and z is the vertical coordinate from the bottom in constant depth $H(0 \leq z \leq H)$; $K_y(z)$ and $K_z(z)$ are the eddy diffusivities for the y-z-directions, respectively, and $c(x,y,z)$ is the concentration of particulate matter. It is assumed that the current speed $u(z)$ is steady and unidirectional, and that diffusion in the direction of current flow is negligible. The boundary conditions are:

$$K_z(z)\frac{\partial c}{\partial z} + w_s c = 0 \qquad z = H,\ x > 0 \qquad (18)$$

$$\frac{\partial c}{\partial z} = 0 \qquad z = 0,\ x > 0$$

$$c = c_o(y,z) \text{ given} \qquad x = 0$$

Solving the above boundary value problem numerically would require long computation times because of the need for large 3-dimensional arrays. The method of moments can be applied to the system to reduce the number of independent variables to two, thereby reducing computation times. The disadvantage of this approach is the loss of some of the detailed information about the concentration field.

The i^{th} moment of $c(x,y,z)$ is defined as:

$$c_i(x,z) = \int_{-\infty}^{+\infty} y^i \, c(x,y,z) \, dy \tag{19}$$

Equations 17 and 18 can be multiplied by y^i and integrated from $-\infty$ to $+\infty$ to yield equations for the i^{th} moment.

The odd moments are zero by symmetry. Most of the information about c is contained in the zeroth and second moments. The zeroth moment represents the number of particles per cm^2 in the xz plane, while the second moment provides a measure of the width of the plume in the transverse (y) direction.

In the original paper, the moment equations are in finite difference form and empirical functions for $K_y(y)$ and $K_z(z)$ are from the literature. The equations were solved numerically, and an example of the results is shown in Figure 16. The vertical distributions of $c_o(x,z)$ are plotted for various times after particle release.

Model 2: Simulation Approach

One disadvantage of the diffusion equation model described above is that a constant ocean depth must be assumed. With the simulation model, bathymetry may be taken into account. In addition, the detailed structure of the ocean current may be incorporated into this model instead of assuming a steady unidirectional current.

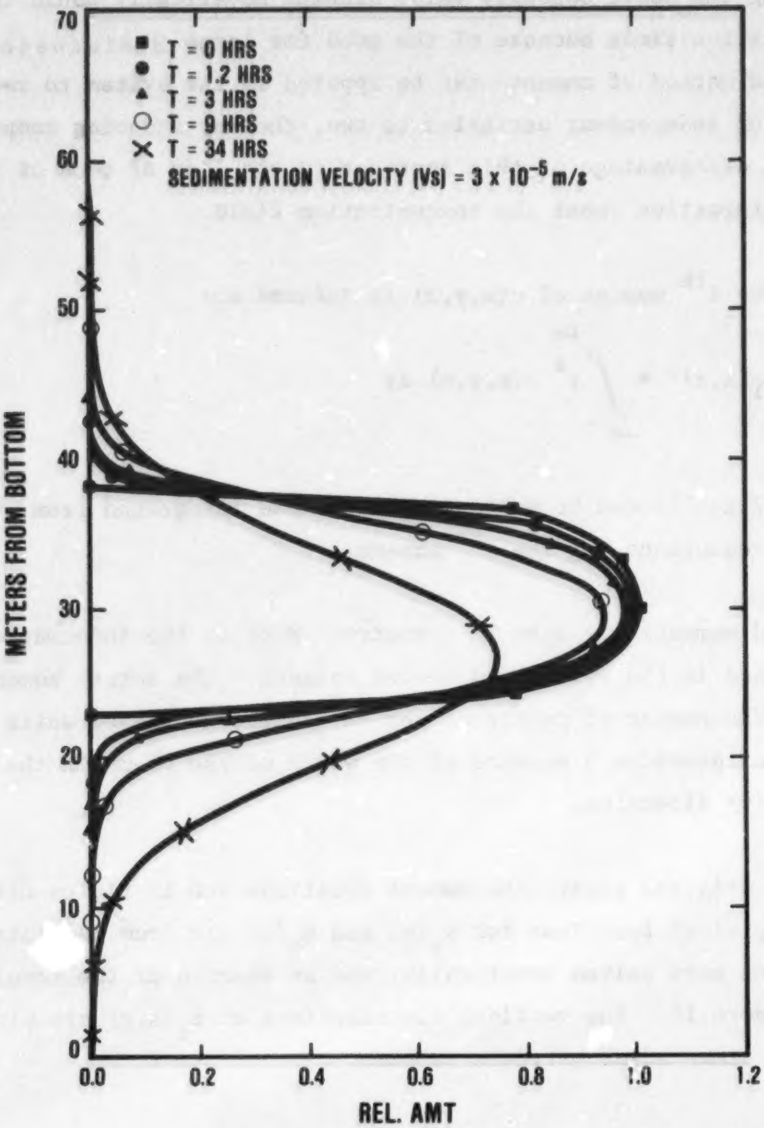

Figure 16. Vertical distribution of particle concentrations at the centerline as a function of travel time.

The basic idea behind the simulation approach is that a particle is carried from its initial location (x_o, y_o, z_o) by longitudinal and transverse ocean currents u and v while it settles with velocity v_s. It eventually reaches the bottom at point (x,y,z_1), where z_1 is the height of the ocean bottom at (x,y) above some reference height (such as the greatest depth in the xy range of interest). All of the detailed information about ocean currents is contained in u and v. The path of the particle transported by u and w while settling at a velocity v_s can be obtained using a digital computer.

The difficulty with this method is that detailed data on ocean currents are lacking. It is therefore necessary to synthesize data by a variety of methods, in addition to using the limited data available. An example of synthetically generated ocean current data is shown in Figure 17.

Although the simulation approach can be adapted to include bathymetry, it will be presented here only for the case of a constant ocean depth. A discussion of modifying the procedure for variable depths is included in the original paper.

The goal of this model is to obtain the bottom fallout pattern B(x,y) at z = 0. This is accomplished by defining probability density functions (pdf) for several variables and integrating these pdf's numerically. Table 17 defines the various probabilities.

TABLE 17. PROBABILITY DEFINITIONS

g(z)dz	probability that a particle emitted by the outfall is at an elevation between z and (z + dz) after the dynamic plume behavior has subsided

(Continued)

TABLE 17. PROBABILITY DEFINITIONS (Continued)

$f(v_s)dv_s$	fraction of particles with settling velocities between v_s and $(v_s + dv_s)$
$c(x_o,y_o,z_o;x,y;v_s)$	probability that a particle initially at (x_o,y_o,z_o) with settling velocity v_s will settle to the bottom position (x,y)
$h(t)dt$	probability that a particle emitted by the outfall will have a fall time between $(t + dt)$

The bottom fallout pattern resulting from a continuous injection of particles is given by:

$$B(x,y) = \iiiint c(x_o,y_o,z_o;x,y;v_s)\ f(v_s)\ dv_s\ g(z_o)\ dz_o S(x_o,y_o)dx_o dy_o \qquad (20)$$

where $s(x_o,y_o)$ is the horizontal source distribution. It is assumed that the density functions are mutually independent in the above expression. If $S(x_o,y_o)$ is taken as $\partial(x_o)\ \partial(y_o)$, where ∂ is the delta function, the integral becomes:

$$B_\partial(x,y) = \iint f(w_s)\ g(z_o)\ c_\partial(z_o;\ x,y;v_s)\ dv_s dz \qquad (21)$$

It is possible to combine the variables z and v_s into the fall time t:

$$t = z/v_s \text{ where } h(t) = \frac{1}{t^2} \int_o^H f(z/t)g(z)zdz, \qquad (22)$$

where h(t) is the density function for fall time. Then the expression becomes:

$$B_\partial(x,y) = \int_0^\infty h(t)\ c_\partial\ (x,y,t)\ dt \qquad (23)$$

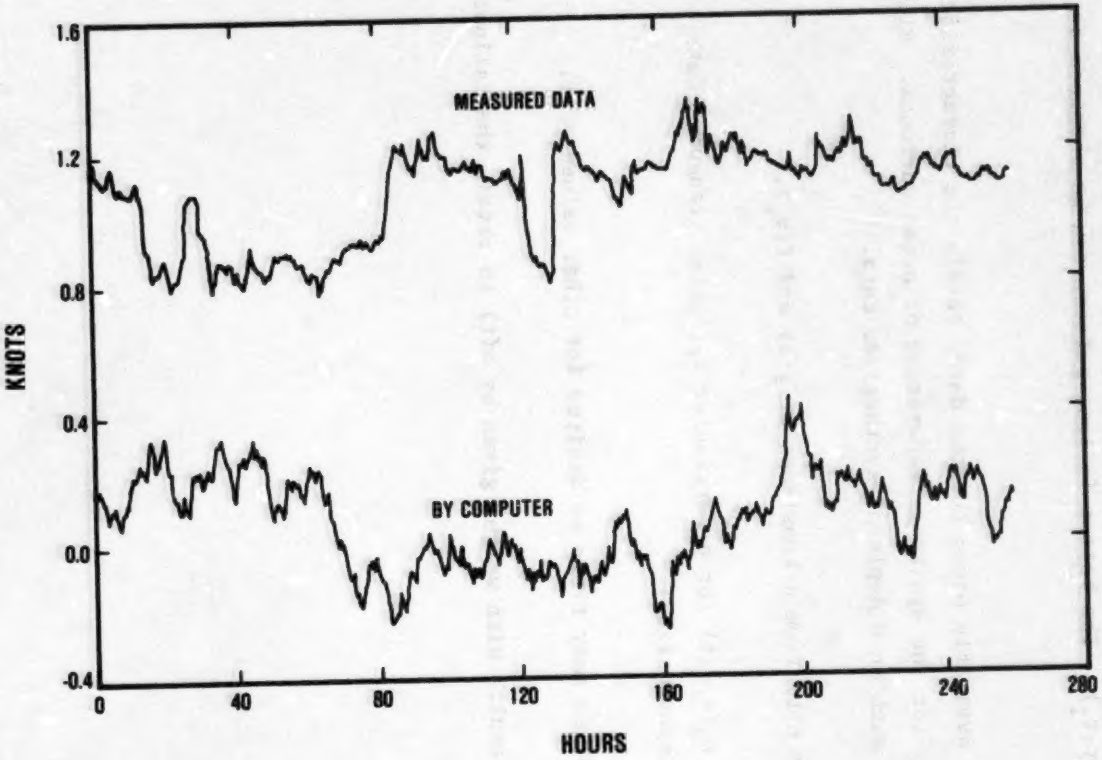

Figure 17. Measured and computer-synthesized ocean current data off White's Point, California.

where $c_\partial(x,y,t)$ represents the probability that a particle will have a horizontal displacement (x,y) in time t. The function $c_\partial(x,y,t)$ can be estimated from particle-release experimental or simulated data. If particles are released into the ocean at time $t = 0$, $x = y = 0$, and $z > 0$, then the positions of the particles at time t_1 in the xy plane can be used to determine $c_\partial(x,y,t_1)$. The bottom fallout pattern can be obtained as follows:

1) From the available ocean current data, obtain the characteristics necessary for the synthetic generation of ocean currents. Figure 17 shows such an example of synthesized data.

2) Determine $h(t)$ from a knowledge of $g(z)$ and $f(v_s)$.

3) Estimate $c_\partial(x,y,t)$ for a particular t_1, using transport data (real or synthesized).

4) Repeat (3) as many times as desired for other values of t.

5) Sum the results with weight given by $h(t)$ to obtain the fallout pattern.

SECTION VI

CONCLUDING REMARKS

The material balance-flow pathway approach presented in this report is general in nature and can be applied to most environmental pollutants in different urban areas. Although the method does not reveal the details of pollutant dispersion in the environment, the requirement of a mass balance demands that all important environmental pathways be identified and quantified. Runoff and long distance transport will affect the inflows of pollutants downstream or downwind of the boundaries of an urban region. Thus, the control of emissions in one region can materially affect inflows into adjacent regions. This accounting method, then, is potentially a powerful tool in assessing the environmental impact of a pollutant. Unfortunately, however, large uncertainties will exist for both input and output terms in the mass balance because of deficiencies in data bases. Refinement of this approach will require more detailed source characterizations and a better theoretical and experimental understanding of particle removal processes in the atmosphere.

SECTION VII

REFERENCES

Allen, G. L., Viets, F. H., and McCabe, L. C., Bureau of Mines Information Information Circular 7627, U.S. Dept. of Interior, Washington, D.C. (1952).

Anthanassiadis, Y. C., "Air Pollution Aspects of Cadmium and Its Compounds," NAPCA Report PB 188 086, APTD 69-32 (1969).

Atkins, P. R., *J.APCA*, *19*, 591 (1969).

Bowen, D. H. M., "Waste Lube Oils Pose Disposal Dilemma," *Environ. Sci. Technol.*, *6*, 25 (1972).

Brewer, P. G., "Minor Elements in Seawater," in *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. *1* (1975).

Brief, R. S., *Arch. Env. Health*, *5*, 527 (1962).

Bruland, K. W., Bertine, K., Koide, M., and Goldberg, E. D., *Environ. Sci. Technol.* *8*, 425 (1974).

Bullas, D. O., 1953, data published by Chamberlain, A. C. (1960).

Bullock, J., and Lewis, W. M., *Atmos. Env.*, *2*, 517 (1968).

Cahill, T. A. and Feeney, P. J., "Contribution of Freeway Traffic to Airborne Particulate Matter," University of California, Davis, UCD-CNL 169, Final Report to the California Air Resources Board (1973).

California State Board of Equalization, *Motor Vehicle Fuel (Gasoline) Distributions*, Department of Business Taxes (1972).

Cannon, H. L., and Bowles, J. M., *Science*, *137*, 765 (1962).

Cardina, J. A., *Rubber Chem. and Tech.*, *47* 1005 (1974).

REFERENCES (Continued)

Carey, R. T. (Ed.), "California County Fact Book 1973," (County Supervisors Association of California, California County Government Education Foundation, 1973). The actual percentage of California vehicles in the metropolitan parts of Los Angeles and Orange Counties is somewhat less than 41.4 because not all of the two counties are included in the study region. The excluded areas are sparsely populated, however, and do not contribute significantly to the automobile population.

Chamberlain, A. C., "Aspects of Deposition of Radioactive and other Gases and Particles," in *Aerodynamic Capture of Particles*, E. G. Richardson, ed, Permagon Press, New York (1960).

Chamberlain, A. C., *Proc. Roy. Soc.*, *296*, 45 (1966).

Chamberlain, A. C., *Proc. Roy. Soc.* *296*, 45 (1967a).

Chamberlain, A. C., *Contemp. Phys.*, *8*, 561 (1967b).

Chamberlain, A. C., "Travel and Deposition of Lead Aerosols," Environmental and Medical Sciences Division, UKAEA Research Group, Harwell (February 1974).

Cholak, J., Schafer, L. J. and Yeager, D., *Amer. Ind. Hyg. Assoc. J.*, *29*, 562 (1968).

Chow, T. J., *Nature*, *225*, 295 (1970a).

Chow, T. J., "Environmental Pollution from Industrial Lead," International Conference on Geochemistry and Hydrochemistry, Tokyo, (1970b).

Chow, T. J., Burland, K. W., Bertine, K. K., Soutar, A. Koide, M., Goldberg, E. D., *Science*, *181*, 551 (1973).

City of Los Angeles, Department of Public Works, "Technical Report: Waste Discharges to the Ocean" (January 1973).

Colucci, J. M., Begeman, C. R., and Kumler, K., *J. APCA*, *19*, 255 (1969).

County Sanitation Districts of Orange County, "Technical Report for Water Quality Control Plan Ocean Waters of California" (January 1973).

Daines, R. H., Motto, H., and Chilko, D. M., *Environ. Sci. Technol.*, *4*, 318 (1970).

Danielson, J. A., Ed., "Air Pollution Engineering Manual" EPA Report 4 AP-40, Second Edition (1973).

Dannis, M. L., Symposium on Ecology, ACS Rubber Division, Toronto, Ontario, May (1974a).

Dannis, M. L., Rubber Chem. and Tech., 47, 1011 (1974b).

Davidson, D. I., Huntzicker, J. J., and Friedlander, S. K., "The Flow of Trace Elements Through the Los Angeles Basin: Impact on Nonurban Areas," Division of Enviromental Chemistry, 167th Meeting, ACS, Los Angeles, Calif. (March 1974).

Dedolph, R., Ter Haar, G., Holtzmann, R., and Lucas, H., Jr., Environ. Sci. Technol, 4, 217 (1970).

DeMarrais, G. A., Holtzworth, G. C., and Hosler, C. R., "Meteorological Summaries Pertinent to Atmospheric Transport and Dispersion over Southern California," Technical Paper No. 54, U.S. Weather Bureau, Washington, D.C. (1965).

Federal Register, "Control of Air Pollution from New Motor Vehicles and New Motor Vehicle Engines," 33, No. 2, Part II, Department of Health, Education, and Welfare (January 1968).

Federal Register, ibid, 33, No. 188 (1968).

Flesch, J. P., Norris, C. H., and Nugent, Jr., A. E., Amer Ind Hyg Assoc. J., 28, 507 (1967).

Friberg, L., Piscator, M., Nordberg, G., "Cadmium in the Environment," CRC Press, Cleveland, Ohio (1971).

Friberg, L., Piscator, M., Nordberg, G. F., and Kjellstrom, T., Cadmium in the Environment, 2nd edition, CRC Press, Cleveland, Ohio (1974).

Friedlander, S. K., Smoke, Dust, and Haze: Fundamentals of Aerosol Behavior, John Wiley and Sons, Inc., New York, New York (1976).

Fulkerson, W. and Goeller, H. E. (eds) "Cadmium: the Dissipated Element" Oak Ridge National Lab. Report ORNL-NSL-EP-21 (1973).

Ganley, J. T., and Springer, G. S., Environ. Sci. Technol., 8, 340 (1974).

Gillette, D. A., and Winchester, J. W., "A Study of Aging of Lead Aerosols," Univ. of Mich. special report, Department of Meteorology and Oceanography (February 1970).

REFERENCES (Continued)

Goetz, A., Stevenson, H. J. R., and Preining, O., J. APCA, 17, 664 (1967).

Gregory, P. H., Microbiology of the Atmosphere, Leonard Hill Books, Ltd., London, 1961, pp. 63

Habibi, K., Environ. Sci. Technol., 4, 239 (1970).

Habibi, K., Environ. Sci. Technol., 7, 223 (1973).

Harrison, P. R., Matson, W. R., and Winchester, J. W., Atmos. Env. 5, 613 (1971).

Heichel, G. H., and Hankin, L., Environ. Sci. Technol., 6, 1121 (1972).

Hering, S. V., unpublished data for lead obtained with a modified Battelle low pressure impactor, Caltech (1975).

Herring, W. O., EPA Report PB-201 739, APTD-0706 (1971).

Hidy, G. M., "Characterization of Aerosols in California," Interim Report for Phase I, State of California Air Resources Board Contract No. 358 (1973).

Hidy, G. M., "Characterization of Aerosols in California," Final Report, Vol II, State of California Air Resources Board Contract No. 358 (1974).

Hidy, G. M., Mueller, P. K., Wang, H. H., Karney, J., Twiss, S., Imada, M., and Alcocer, A., J. Appl. Meteor., 13, 96 (1974).

Hirschler, D. A., Gilbert, L. F., Lamb F. W., and Niebylski, L. M., Ind. Eng. Chem., 49 1131 (1957).

Hirschler, D. A., and Gilbert, L. F., Arch. Environ. Health, 8, 297 (1964).

Huntzicker, J. J., Davidson, C. I., and Friedlander, S. K., "The Flow of Trace Elements throughout the Los Angeles Basin: Zn, Cd, and Ni," Division of Environmental Chemistry, 167th Meeting, ACS, Los Angeles, California (March 1974).

Huntzicker, J. J., and Davidson, C. I., "Atmospheric Trace Metal Flows in the Los Angeles Basin: Zn, Cd, and Ni," in "Air-Water-Land Relationships for Selected Pollutants in Southern California," Huntzicker, J. J., Friedlander, S. K., and Davidson, D. I., Ed., Final Report to the Rockfeller Foundation, Caltech (August 1975).

REFERENCES (Continued)

Huntzicker, J. J., Friedlander, S. K., and Davidson, C. I., "A Material Balance for Automobile Emitted Lead in the Los Angeles Basin," Environ. Sci. Technol. 9, 448-457 (1975a).

Huntzicker, J. J., Friedlander, S. K., and Davidson, C. I., "Air-Water-Land Relationships for Selected Pollutants in Southern California," Final Caltech Report to the Rockefeller Foundation (August 1975b).

Islitzer, N. F., and Dumbauld, R. K., Int. J. Air Wat. Poll., 7, 999 (1963).

Kloke, A., and Riebartsch, K., Die Naturwissenshaften, 51, 367 (1964).

Lagerwerff, J. V., and Specht, A. W., Environ. Sci. Technol., 4, 583 (1970).

Lazrus, A. L., Lorange, E., and Lodge, Jr., J. P., Environ. Sci. Technol., 4, 55 (1970).

Lee, Jr., R. E., Patterson, R. K., and Wagman, J., Environ. Sci. Technol., 2, 288 (1968).

Lee, Jr., R. E., Patterson, R. K., Crider, W. L., and Wagman, J., Atmos. Env., 5, 225 (1971).

Lee, Jr., R. E., and von Lehmden, D. J., J. APCA, 23, 853 (1973).

Lee, Jr., R. E., and Goranson, S. S., "Variations in the Size of Airborne Particulate Matter over a Three-Year Period," 68th Annual Meeting, AIChE, Los Angeles (November 1975).

Lees, L., "Smog--A Report to the People," Environmental Quality Laboratory, California Institute of Technology, Pasadena, California (1972).

Leh, H. O., Gesunde Pflanzen, 18, 21 (1966).

Lemke, E. E., "Profile of Air Pollution Control," Air Pollution Control District, County of Los Angeles (1971).

Lininger, R. L., Duce, R. A., Winchester, J. W., and Matson, W. R., J. Geophys. Res., 71 2457 (1966).

Lundgren, D. A., J. APCA, 20, 603 (1970).

Lundgren, D. A., and Paulus, H. J., "The Mass Distribution of Large Atmospheric Particles--and how it Relates to What a High Volume Sampler Collects," 66th Annual Meeting, Air Pollution Control Association, Chicago, Illinois (June 1973).

REFERENCES (Continued)

Lundgren, D. A., and Paulus, J. J., "Direct Determination of the Total Atmospheric Mass Distribution," Division of Environmental Chemistry, 167th Meeting, ACS, Los Angeles, Calif. (March 1974).

Marple, V. A., and Liu, B. Y. H., Environ. Sci. Technol., 8, 648 (1974).

Marple, V. A., Liu, B. Y. H., and Whitby, K. T., Aerosol Sci, 5, 1 (1974).

Marten, G. C., and Hammond, P. B., Agron. J., 58, 553 (1966).

May, K. R., Applied Microbiology, 12, 37 (1964).

McCrone, W. C., and Delly, J. G., Particle Atlas, Edition 2, Volume 2, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1973).

Megaw, W. J., and Chadwick, R. C., 1957, data published by Chamberlain, A. C. (1960).

Milde, R. L. and Beatty, H. A., in "Metal-Organic Compounds," Advances in Chemistry Ser., No. 23, 306, ACS, Washington, D. C. (1959).

Moran, J. B., and Manary, O. J., "Effect of Fuel Additives on the Chemical and Physical Characteristics of Particulate Emissions in Automotive Exhaust Interim Technical Report to the National Air Pollution Control Administration," Dow Chemical Co., APTD 0618, PB 196 783 (1970).

Motto, H., Daines, R., Chilko, D., and Motto, C., Environ. Sci. Technol., 4, 231 (1970).

Mueller, P. K., Helwig, H. L., Alcocer, A. E., Gong, W. K., and Jones, E. E., ASTM Special Tech. Publication No. 352, 60 (1964).

National Air Surveillance Networks, Environmental Protection Agency Report PB 224 823 APTD 1467 (1973).

Ninomiya, J. S., Bergman, W., and Simpson, B. H., in "Proceedings of the Second International Clean Air Congress," H. M. Englund and W. T. Beery, Ed., Academic Press, New York (1971).

Ondov, J. M., Zoller, W. H., and Gordon, G. E., "Trace Elements on Aerosols from Motor Vehicles," presented at the Air Pollution Control Association Annual Meeting, Denver, Colorado (June 1974).

Page, A. L., Ganje, T. J., and Joshi, M. S., Hilgardia, 41, 1 (1971).

Parkhurst, J. D., "Technical Report: Waste Discharge to the Ocean," Sanitation Districts of Los Angeles County (January 1973).

Patterson, C. and Settle, D., "Contribution of Lead via Aerosol Deposition to the Southern California Bight," Journal de Recherche Atmospheriques (1974).

Patterson, C. C., and Elias, R., unpublished data, 1975.

Peirson, D. H., Cawse, P. A., Salmon, L., and Cambray, R. S., Nature, 241, 252 (1973).

Peirson, D. H., 1973, published in Chamberlain, A. C. (1974).

Pierson, W. R., and Brachaczek, W. W., Rubber Chem and Tech, 47, 1275 (1974).

Pitt, R. E. and Amy, G., "Toxic Materials Analysis of Street Surface Contaminants," Environmental Protection Agency Report EPA-R2-73-283 (1973).

Public Health Service, Division of Air Pollution, U. S. Department of Health, Education, and Welfare, "Survey of Lead in the Atmosphere of Three Urban Communities," PHS 999-AP-12 (1965).

Purdue, L. J., Enrione, R. E., Thompson, R. J., and Bonfield, B. A., Anal. Chem. 45, 527 (1973).

Rabinowitz, M., Chemosphere, 4, 175 (1972).

Rains, D. W., and Thornton, S., "Vegetation as an Indication of Long-Term Lead Pollution, Its Extent and Effect," University of California, Davis, California (1970).

Rao, A. K., "An Experimental Study of Inertial Impactors," Ph.D. Thesis under K. T. Whitby, Particle Technology Laboratory, Mechanical Engineering Department, University of Minnesota (June 1975), pg. 100.

Raybold, R. L., Byerly, R., Jr., "Investigation of Products of Tire Wear," NBS Report 10834 (April 1972).

Roberts, P. J. W., Roth, P. M., and Nelson, C. L., "Contaminant Emissions in the Los Angeles Basin," Appendix A of "Development of a Simulation Model for Estimating Ground Level Concentrations of Photochemical Pollutants," Report 71 SAI-6, Systems Applications, Inc., Beverly Hills, California (1971).

Robinson, E., and Ludwig, F. L., J. APCA, 17, 664 (1967).

Rolfe, G. L., and Haney, A., "An Ecosystem Analysis of Environmental Contamination by Lead," University of Illinois at Urbana-Champaign, Institute for Environmental Studies, Metals Task Force Research Report No. 1 (August, 1975).

REFERENCES (Continued)

Sanitation Districts of Los Angeles County, "Technical Report: Waste Discharge to the Ocean" (January 1973).

Schuck, E. A., and Locke, J. K., Environ. Sci. Technol., 4, 324 (1970).

Sehmel, G. A., J. Geophys. Res., 75, 1966 (1970).

Sehmel, G. A., in "Assessment of Airborne Particles," T. T. Mercer, P. E. Morrow, W. Stober, Ed., Charles C. Thomas, Springfield, Illinois (1972).

Sehmel, G. A., J. Aerosol Sci., 4, 125 (1973).

Sehmel, G. A., Sutter, S. L., and Dana, M. T., "Dry Deposition Processes," Battelle NW Laboratory Paper 1751 Part 1 (1973).

Servant, J., "Deposition of Atmospheric Lead Particles to Natural Surfaces in Field Experiments," Conference of Atmosphere-Surface Exchange Processes, Richland, Washington (September 1974).

Servant, J., "Le Bilan Hydrometeorologique du Plomb sur la France" (1972-3). "Considerations sur le Bilan et Importance du Depot Sec.," International Conference on Trace Metals in the Environment, Toronto (October 1975).

Shelton, E. M., "Motor Gasolines, Winter 1971-72," Mineral Industry Surveys, Petroleum Products Survey, No. 75, U. S. Department of the Interior, Bureau of Mines (June 1972).

Southern California Coastal Water Research Project (SCCWRP), "The Ecology of the Southern California Bight: Implications for Water Quality Management," SCCWRP TR104 (1973).

Southern California Coastal Water Research Project, Annual Report, El Segundo, California (1974).

Southern California Coastal Water Research Project, Annual Report, El Segundo, California (1975).

Southern California Coastal Water Research Project, Annual Report, El Segundo, California (1976).

State of California, "Implementation Plan for Achieving and Maintaining the National Ambient Air Quality Standards" (January, 1972).

State of California Water Resources Control Board, "Water Quality Control Plan for Ocean Waters of California" (July 6, 1972).

REFERENCES (Continued)

Tepper, L. B., "Seven-City Study of Air Pollution Lead Levels: An Interim Report," Environmental News, U.S. Environmental Protection Agency, June 4, 1971.

Ter Haar, G., Env. Sci. and Tech., 4, 226 (1970).

Ter Haar, G. L., Lenane, D. N., Hu, J. N., and Brandt, M., J. Air Pollut. Control Assoc. 22, 39 (1972).

Tufts, B. J., Analytical Chem., 31, 238 (1959).

U.S. Department of Commerce, "Climatological Data, California," National Oceanic and Atmospheric Administration, Environmental Data Service (1968-1973).

U.S. Geological Survey, "Water Resources Data for California, Part 2, Water Quality Records," U.S. Dept. of Interior (1973, 1974, 1975).

Watson, H. H., Amer. Ind. Hyg. Assoc. J., 15, 5 (1954).

Weinstock, B., and Niki, H., Science 176, 290 (1972).

Wilson, W. E., Jr., J. Phys. Chem. Ref. Data, 1, 535 (1972).

Zimdahl, R. L., in "Impact on Man of Environmental Contamination Caused by Lead," H. W. Edwards, Ed., Colorado State University, NSF Grant GI-4 Interim Report (1972).

☆U.S. GOVERNMENT PRINTING OFFICE: 1978 - 786-068/1245 Region No. 9-1